

TREASURY DEPARTMENT  
UNITED STATES PUBLIC HEALTH SERVICE  
HUGH S. CUMMING, SURGEON GENERAL

**STUDIES ON OXIDATION-REDUCTION**

**IX. A POTENTIOMETRIC AND SPECTROPHOTOMETRIC  
STUDY OF MERIQUINONES OF THE P-PHENYLENE  
DIAMINE AND THE BENZIDINE SERIES**

BY

W. MANSFIELD CLARK  
*Chief of Division of Chemistry*

BARNETT COHEN  
*Chemist*

AND

H. D. GIBBS  
*Senior Chemist*  
*Hygienic Laboratory, United States Public Health Service*

---

SUPPLEMENT No. 54  
TO THE  
PUBLIC HEALTH REPORTS



WASHINGTON  
GOVERNMENT PRINTING OFFICE  
1926

ADDITIONAL COPIES  
OF THIS PUBLICATION MAY BE PROCURED FROM  
THE SUPERINTENDENT OF DOCUMENTS  
GOVERNMENT PRINTING OFFICE  
WASHINGTON, D. C.  
AT  
10 CENTS PER COPY

## CONTENTS

---

I. Introduction.....	Page 1
II. Orienting experiments.....	3
o-Tolidine.....	3
Benzidine.....	9
Benzidine trisulfonate.....	11
Dichloro-o-tolidine.....	11
Wurster's red.....	11
p-Phenylene diamine.....	17
Wurster's blue.....	17
III. Theoretical equations.....	17
IV. Completing data.....	24
Absorption spectra.....	25
o-Tolidine.....	29
Wurster's red.....	30
Wurster's blue.....	34
V. General discussion.....	37
VI. Summary.....	43
VII. Tables.....	46
VIII. References.....	60

the  
noti-  
th

---

the  
noti-  
th



## STUDIES ON OXIDATION-REDUCTION

### IX. A POTENTIOMETRIC AND SPECTROPHOTOMETRIC STUDY OF MERIQUINONES OF THE P-PHENYLENE DIAMINE AND THE BENZIDINE SERIES<sup>1</sup>

#### I. Introduction

Reversible oxidation-reduction in simple quinone-quinol systems has been successfully subjected to the potentiometric method of study. Within recent years there have appeared a number of papers on the subject. References to these are given in a recent review by Clark (1925). Comparable data upon analogous diamine-diimine systems of either the phenylene diamine or benzidine type have not appeared in the literature.

If such experimental projects have been contemplated, it is not improbable that they have been inhibited by knowledge of the instability of the oxidants. For instance, the early attempts to isolate the simplest quinone diimine from the products of ordinary oxidation of p-phenylene diamine were unsuccessful; but Willstätter and Mayer (1904) obtained it by reducing quinone dichlorodiimine with HCl and separating it from the dry ethereal solution. The knowledge thus gained enabled Willstätter and Pfannenstiel (1905) to prepare the diimid directly from the reductant, p-phenylene diamine; but one of the conditions was the avoidance of moisture.

The instability of quinone diimine in aqueous solution is characteristic in varying degrees of other similar compounds according to abundant chemical evidence which we shall confirm in specific instances with physical measurements. Consequently, there is little hope of finding among the simpler members of these groups of compounds systems well adapted to the demonstration of first principles in the application of potentiometric methods.

However, the systems to be discussed have been rather extensively used in biochemical studies, and knowledge of their conduct is fundamental to an understanding of a wide variety of important problems. It is, therefore, important to determine whether or not potentiometric studies can be of use in defining any characteristics of these systems.

Of particular interest is the bearing of new experimental data upon the puzzling problem of meriquinones.

It was known for a long time that partial oxidation of the diamines now under consideration produces remarkably brilliant colored solutions. After Willstätter and his students had sufficiently mastered the products of full oxidation, he and Piccard (1908) were able to

<sup>1</sup> Manuscript submitted for publication Dec. 29, 1925.

show that the brilliantly colored products of partial oxidation are comparable with the quinhydrones in which color is enhanced by the mixing of the yellow quinone with the colorless hydroquinol. Not wishing to imply that the colored, crystalline compounds which can be isolated from solutions of partially oxidized diamines are in all cases composed of equimolecular parts of oxidant and reductant, Willstätter and Piccard named them *meriquinones*, i. e., *partial oxidation products*. The fully oxidized products they termed *holoquinones*.

These meriquinones are difficult to account for by the application of simple valence rules; but the fact of definite constitution, the occurrence of the separable oxidant and reductant in the same crystal, and the brilliancy of color and its modification by substitutions have stimulated new speculations upon the perennial subject of color in its relation to molecular constitution.

Perhaps the numerical data to be found in this paper will be a definite contribution to this subject.

In surveying a limited number of systems we have found the system of para amino dimethyl aniline, a representative of the phenylene-diamine series, and that of o-tolidine, a representative of the benzidine series, to be the more suitable to our methods. No exhaustive study has been made of either; but what has been accomplished with these systems and incidental experiments with similar systems will furnish a rough outline of the type of phenomena to be encountered.

As the theme develops, it will become clear that these phenomena are complex. Therefore, we have attempted to clarify the presentation by restricting the next section (II) of this paper to experiments for which the ordinary type of equation is applicable. Titrations at constant pH will determine the relation of potential to percentage oxidation in accordance with the equation

$$E_h = E'_o - 0.03006 \log \frac{[S_r]}{[S_o]} \quad (a)$$

Experiments with solutions equimolecular with respect to total reductant  $[S_r]$  and total oxidant  $[S_o]$  will reveal the effects of pH change and furnish data for equation (b),

$$E_h = E_o + 0.03006 \log \frac{K_{r1}K_{r2} + K_{r2}[H^+] + [H^+]^2}{K_{o1}K_{o2} + K_{o2}[H^+] + [H^+]^2} - 0.0601 \text{ pH} \quad (b)$$

Here  $K_{r1}$  = first ionization constant of reductant;  
 $K_{r2}$  = second ionization constant of reductant;  
 $K_{o1}$  = first ionization constant of oxidant;  
 $K_{o2}$  = second ionization constant of oxidant;  
 each defined as shown on page 17.

The conditions which permit the restricted application of equations (a) and (b) will become evident in the third section, where there is assembled a systematic development of equations descriptive of these peculiar oxidation-reduction systems. From this there can be predicted certain phenomena which are confirmed in a rough way by the special experimental data described in Section IV.

The preliminary survey thus extended will be found far from complete, and yet sufficient to serve as a guide to certain conclusions drawn in Section V.

All experiments were performed at 30° C.; hence the numerical coefficients used in (a) and (b).

The buffer solutions, unless others are specifically mentioned, were those recorded in Table 4 of the eighth paper of this series. Since most buffer solutions contain anions which are subject to specific reaction with bases such as those now under consideration, we were apprehensive. But in the dilutions of the bases employed, at the pH values used, and within the very limited time period of each experiment, we observed nothing which would lead us to suspect that the nature of the buffer solutions invalidate the data.

The oxidizing agent to be employed should not combine with the bases to form insoluble salts. It will become evident that in oxidizing the reductants in question, an agent belonging to a system of high characteristic potential is necessary. It will also become evident that the oxidizing agent must be one of rapid action. Chlorine water fulfilled the requirements.

Gold-plated electrodes were found to be too sluggish for the purpose and were abandoned without further study. Instead, bright platinum electrodes were used. Substantial agreement was found in cases where drifts of potential were sufficiently slow to permit comparison of two electrodes. In most cases, however, the rapidity with which measurements had to be made precluded observations of more than one electrode.

## II. Orienting Experiments

### O-TOLIDINE

The o-tolidine used in the experiments was a sample from the Research Laboratory of the Eastman Kodak Co.

In Table 1 (at the end of this paper) are shown the changes of potential with time at three different values of pH. The initial 50 per cent oxidation was induced by adding the calculated amount of chlorine-water to the buffered solution 0.00009 molar with respect to o-tolidine. The zero time of Table 1 was that of the first instant at which potentiometer balance could be obtained. This did not require more than about 20 seconds.

In solutions more alkaline than pH 4.4 the changes of potential become too rapid to be followed with accuracy, and are not apparently lowered to a new order of magnitude by lowering the temperature; but in the most acid solution the stability for a limited period of time is sufficient to permit measurement of potentials at successive stages of oxidation. Thus there was obtained the ordinary "titration curve" at constant pH. Furthermore, in solutions of the acidity used, equation (a), page 2, should hold.

It will later be shown that an exactly half oxidized solution when carried through solutions of different pH value should exhibit potentials in accordance with equation (b), page 2.

In Tables 2 to 7 equation (a) is shown to hold with an approximation sufficient for purposes of outline.

Incidentally, the data demonstrate with reasonable certainty that two equivalents are concerned, and that these are somehow paired in their energetics (*cf.* Paper V, this series).

In Table 2 the end point of 10 c. c. chlorine water was estimated from the concentrations of o-tolidine and chlorine. In Tables 3 to 7 the end points were estimated from the potential change, the standardization of the chlorine-water being only approximate. In the experiment summarized in Table 7 the pH of the buffer solution was such that important changes probably occurred during the 18 minutes required for the experiment. This, perhaps, led to the choice of a wrong end point and invalidated the accuracy of the individual readings at successive steps of oxidation. Furthermore, accurate comparison of the final characteristic  $E_o$  value with those of Tables 2 to 6 would involve small but appreciable corrections which will appear later. Therefore the close agreement with the other  $E_o$  values is partly accidental; but the errors and corrections at this pH level are still not large enough seriously to injure the gross significance of the value found.

In Tables 2 to 7 the potential  $E_o$  of an equimolecular mixture of oxidant and reductant at pH=0 is calculated by subtracting from the average  $E'_o$  value in each case the hydrogen electrode potential ( $\pi_h$ ) of the buffer used.  $E'_o$  is the potential of an equimolecular mixture of oxidant and reductant at a particular pH value. The fact that  $E_o$  values so calculated agree substantially shows that the  $E'_o$ :pH curve has the frequently occurring ".06-slope" in this region.

The average of the  $E_o$  values, 0.8723, 0.8726, 0.8712, 0.8731, 0.8731, and the doubtful last value 0.8735 is 0.8726. In good agreement with this average are the average values of Tables 8, 9, and 10, namely, 0.872, 0.872, and 0.873. The latter were obtained in the course of measurements planned to show the variation of the potential of a fixed mixture of oxidant and reductant with variation of pH. Each of these series of measurements included a titration

which furnished the means for calculating the ratio of reductant to oxidant in each individual experiment.

In addition, there is the experiment in the most acid solution recorded in Table 1 which admits the application of equation (b) for calculating  $E_o$ . Here again the initial potential and the pH value yield 0.873 for  $E_o$ .

The data of Tables 8, 9, and 10 are the results of experiments designed to reveal the relation of  $E'_o$  to pH. There are included four series of measurements, each conducted as follows. The same measured quantity of o-tolidine solution was added to each of several de-aerated buffer solutions. After a preliminary titration with chlorine in one of the more acid solutions, it was possible to select some convenient quantity of the chlorine-water which would bring about a partial oxidation lying at some definite point between 40 per cent and 50 per cent. This determined quantity of oxidizing agent was then added in turn to each buffered tolidine solution.

At the time when these measurements were made it was not realized that a condition to be met if experiments of this kind are to be interpreted without complications is that  $[S_o]$  must exactly equal  $[S_r]$ . But since this condition was approximated and since the possible errors in its violation in this particular instance are probably not much more than the uncertainties of measurement in the regions of pH concerned, we have not repeated the work.

In the more acid solutions some leisure in potential measurements was permissible; but, for a reason which will presently become evident, initial potentials obtained as soon as potentiometric balance could be reached were used.

We have already shown by Table 1 that the rate of potential change is greatly accelerated by increase in pH, and we have stated that in the more nearly neutral solutions the rate of change is too great for accurate measurement.

Since we found no unique points in the course of the continuous drift of potential, and since initial potentials in the more acid solutions were found to be significant, it was decided to operate as rapidly as possible and to place under consideration the potentiometric readings that were found at the moment when the first potentiometric balance was obtained.

Approximate positions of the potentiometer settings were obtained in a preliminary set of experiments, and then for the final measurements two operators worked as follows: One operator set the potentiometer within about  $\pm 0.03$  volt of the expected reading. The other operator then added the oxidizing agent to the actively stirred tolidine solution and signaled the moment at which the addition was complete. Potentiometric balance was then made as rapidly as



possible to the nearest 0.001 volt, and the reading at the moment of temporary balance was recorded as "initial potential." Now it would seem that data taken under such circumstances should be "thrown out of court" as unreliable. However, we may legitimately examine the data as they stand.

In Figure 1 the "initial potentials" reduced to  $E'_0$  values (potential of an equimolecular mixture of oxidant and reductant at a given pH value) are plotted as ordinates with pH values as abscissas, the o-tolidine data being represented by dots.

In the more acid regions the "initial potentials" fall on the curve AB with ".06-slope" previously described. As neutrality is approached, the "initial potentials," instead of deviating from this ".06-slope" in the direction of the drifts of potential, deviate in the opposite direction and finally fall near a new curve CD of ".06-slope."

It is, of course, possible that, as the pH of the buffer system increases, the drifts of potential become so rapid as to destroy all significance in the "initial potentials," leaving only an apparent order in the data occasioned by some experimental artefact. This possibility we clearly recognize.

Inspecting the experimental data as they stand, we are led on to some interesting facts. The first inflection of the curve is near pH 3 to 4 and is in a direction which, were we dealing with perfectly reliable data, would be expected if there occurred in this region the suppression of the dissociation of a basic reductant. It will be shown later that o-tolidine solutions are amenable to hydrogen electrode measurements, and that the dissociation constants calculated from such measurements are fairly close to those which characterize the inflection of the  $E'_0$ :pH curve now under discussion.

If, however, the dissociations of both groups in the reductant were alone concerned, the inflection should continue until  $\frac{-dE}{dpH}$  became zero near pH 5 to 6. Instead, the  $E'_0$ :pH curve swings back to a ".06-slope."

Both in the preliminary measurements, where no anticipation could have influenced the results, and in the final more rapid measurements, where the potentiometer settings were at random within a broad zone of potential, so uniform an alinement of "initial potentials" was found that an artefact seems rather impossible. It is also improbable that the dissociation constants of the oxidant are either so nearly equal to the known values of the reductant as to obscure the effect of a difference, or so widely different as to be without effect in the pH region under consideration. If, then, we apply the known constants of the reductant, we should expect that the countereffects of dissociation in the oxidant would become

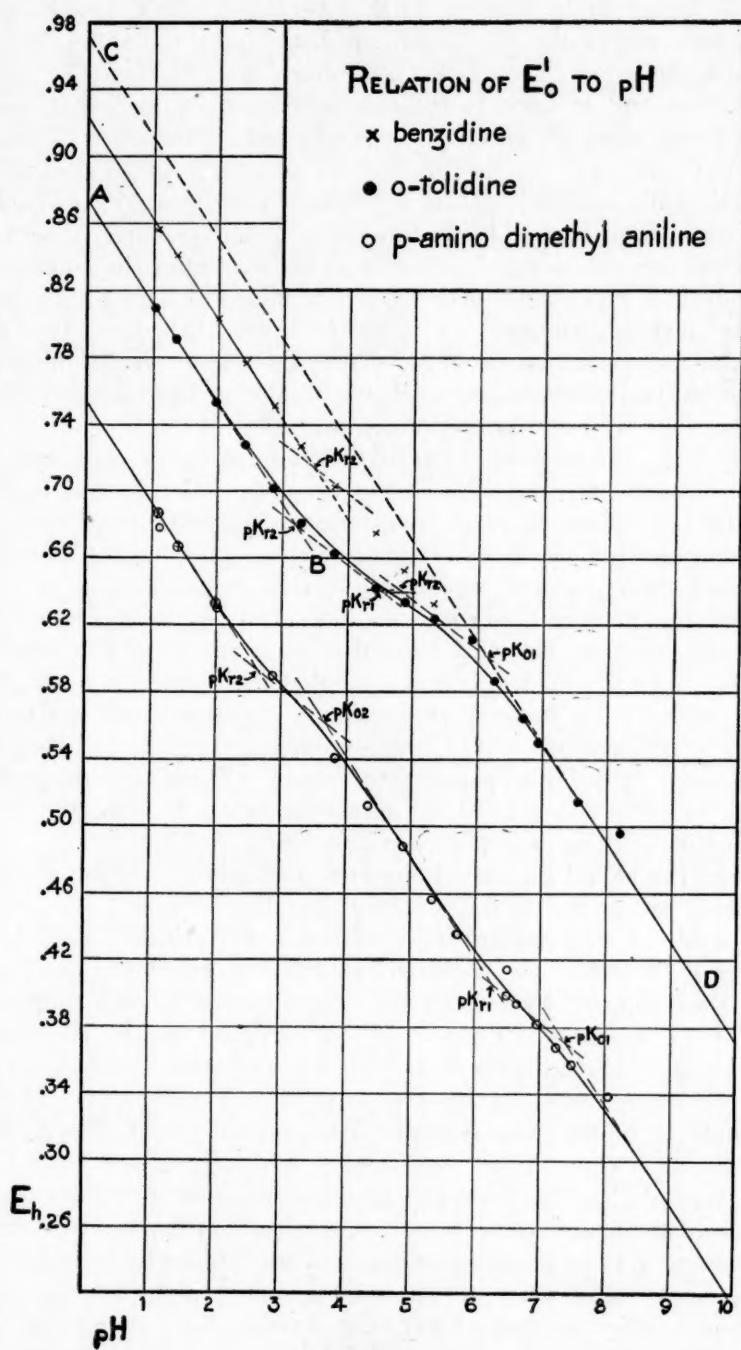


FIG. 1

evident in a near by region of pH. Assuming values for  $pK_0$  and  $pK_2$  which will be described later, we have applied equation (b) to the construction of the curve for o-tolidine shown in Figure 1.

We have had occasion in the past to note the remarkable speed with which electrode equilibria are attained in certain oxidation-reduction systems. In the present instance it is quite clear that "initial potentials," with their indubitable significance in acid solutions, furnish, in less acid solutions, data in fair conformity with a plausible theoretical curve involving two characteristic constants, the values of which agree with those determined by a different experimental method, namely, that of the hydrogen electrode. We may therefore conclude that, in spite of inevitable inaccuracies inherent in the method of operation which we were forced to use, the rough outline of the system has been accomplished.

We shall now consider the hydrogen-electrode measurements. Since approximate determinations of the dissociation constants sufficed for the purpose at hand, no attempt was made to duplicate the salt concentration of the oxidation-reduction experiments in order to obtain values precisely applicable to those conditions.

A solution of o-tolidine with two equivalents of hydrochloric acid was made by dissolving, with the aid of warming, 2.122 g. o-tolidine in 100 c. c. 0.2 N HCl. This was diluted with water to a solution 0.001 molar with respect to o-tolidine dihydrochloride. With a portion of this solution, liquid junction was made in bulb S of the Figure 1 shown in the third paper of this series. Then, after the draining of the parts which had been immersed, vessel A, with 50 c. c. of the tolidine solution, was placed in position.

When the palladium-coated electrode had become saturated with hydrogen, titration with 0.005 normal NaOH was begun.

In Table 11 the results, with the 0.001 molar solution, have been treated as if the 20.6 c. c. NaOH required to reach the end point were that required by 50 c. c. of 0.00103 molar tolidine dihydrochloride. The extra 0.6 c. c. was that required by the undrained liquid and by the diffusion from bulb S. The error of this assumption can be neglected for present purposes. The treatment shown in Table 11 follows Van Slyke's (1922) procedure (*cf.* Hastings & Van Slyke, 1922). There are yielded fairly consistent values of  $pK'_1$  and  $pK'_2$ . These are the apparent dissociation constants as of an acid and should correspond closely with the  $pK_{r1}$  and  $pK_{r2}$  used in Section III in formulating the oxidation-reduction equilibria. Transformation of these to the corresponding and more familiar basic dissociation constants by the use of  $pK_w = 13.73$  shows that the first basic dissociation constant of o-tolidine is  $6.2 \times 10^{-10}$  and the second  $2.9 \times 10^{-11}$ .



In the measurements recorded in Table 11 the two electrodes agreed perfectly during the major course of the titration, exhibiting differences only near the end point, as is frequently the case. There was some evidence of very slow drifts of potential which would have become of significant magnitude only after the lapse of considerable time. Duplicate experiments agreed as well as could be expected of the manipulation of such dilute solutions under only ordinary care. In short, there is nothing apparent in the experiments to preclude their acceptance on the same basis as that of many other titrations of organic acids or bases.

These determinations of the dissociation constants of the reductant (o-tolidine) have been applied in the calculations from which the curve of Figure 1 was drawn. But they would be of limited value to the present discussion unless numerical data for equation (b) could be completed with values for  $K_{o1}$  and  $K_{o2}$ . For these we have no independent data. However, the displacement at constant pH between projections of AB and CD of Figure 1 permits the calculation of the sum  $pK_{o1} + pK_{o2}$ . This we find by graphic approximation to be 11. Assuming that each pK value of the oxidant is displaced from the corresponding value of the reductant by the same amount, or  $pK_{o1} - pK_{r1} = pK_{o2} - pK_{r2}$ , and, knowing that  $pK_{r1} + pK_{r2} = 7.71$ , we find  $pK_{o1} = 6.16$  and  $pK_{o2} = 4.84$ . We have, then, in summary, the following data for the o-tolidine system:

$E_o = +0.873$ ;

$pK_{r1} = 4.52$ , or  $K_{r1} = 3.0 \times 10^{-5}$ , or first basic dissociation constant of reductant  $= 6.2 \times 10^{-10}$ ;

$pK_{r2} = 3.19$ , or  $K_{r2} = 6.5 \times 10^{-4}$ , or second basic dissociation constant of reductant  $= 2.9 \times 10^{-11}$ ;

$pK_{o1} = 6.16$ , or  $K_{o1} = 6.9 \times 10^{-7}$ , or first basic dissociation constant of oxidant  $= 2.7 \times 10^{-8}$ ;

$pK_{o2} = 4.84$ , or  $K_{o2} = 1.4 \times 10^{-5}$ , or second basic dissociation constant of oxidant  $= 1.3 \times 10^{-9}$ .

Of these values, those of  $E_o$  and of the first and second dissociation constants of o-tolidine are fairly reliable. Those of the first and second dissociation constants of the oxidant are crude approximations, the validity of which depends upon the argument we have presented.

#### BENZIDINE

The benzidine system, under the conditions of our experiments, was much more unstable than the o-tolidine. Consequently only enough experiments were made to reveal the order of magnitude of  $E_o$  and to suggest that the relation of  $E'_o$  to pH parallels that of the o-tolidine system.

The benzidine used was an Eastman Kodak Co. product recrystallized as follows.

A saturated solution was made in hot 95 per cent ethanol and filtered rapidly with minimum exposure to air. The filtrate was added to about 10 volumes of de-aerated water and the white flakes of benzidine were filtered off. These crystals were redissolved in warm 80 per cent ethanol and reprecipitated in air-free water. The pearly, white flakes were washed thrice with de-aerated distilled water and dried in a vacuum desiccator over  $\text{H}_2\text{SO}_4$ .

In Tables 12 to 16 are the results of chlorine-water titrations of solutions 0.0001 molar with respect to benzidine, and buffered at the indicated pH values.

These data are summarized under "First series" in Table 17. The remaining values under "First series" and the "Second series" of measurements in Table 17 were obtained under conditions designed to show more fully the relation of  $E'_0$  to pH. These involved only the "initial potentials" obtained directly after the addition of an equivalent of chlorine. Since this procedure allowed less time for disappearance of the oxidation product, the single data are probably as valid as the more detailed measurements of the first series. The average of all values of  $E_0$  in Table 17 is +0.921.

In Figure 1 are shown graphically, by means of crosses, the data of Table 17.

It may be noted that substitution of alkyl groups has the same general effect in these systems that it has in other systems.

Independent calculations of the dissociation constants of benzidine were made from hydrogen electrode measurements. The procedure was comparable to that used in the titration of o-tolidine dihydrochloride. The experimental data and calculations therefrom are shown in Table 18.

The  $\text{p}K_1$  and  $\text{p}K_2$  values of Table 18 on transformation yield  $9.3 \times 10^{-10}$  and  $5.6 \times 10^{-11}$  for the first and second basic dissociation constants, respectively.

Again in the case of benzidine as in the case of o-tolidine we find in the  $E'_0$  : pH curve an inflection. The position of this corresponds to the experimentally determined value of a dissociation constant for the reductant. It is in a region of pH where there still remains a fair degree of certainty in the potential measurements. But with benzidine the measurements in the more nearly neutral solutions were so very uncertain that we shall no more than record the facts as found and show in Figure 1 the suggestion of a parallelism between the case of tolidine and that of benzidine.

The colors at different pH values seem also to parallel those of the tolidine system, but in their more rapid fading they reveal the greater instability of the benzidine system.

## BENZIDINE TRISULFONATE

Doctor Sullivan, of this laboratory, prepared for us a sample of benzidine trisulfonate by the method of Griess and Duisberg (1889). On following the alkali titration of this material by means of hydrogen electrode measurements, an end-point was observed which could be accounted for on the assumption that about 96 per cent of the material was a trisulfonic acid of which all three sulfonic acid groups are very strong. This percentage agreed substantially with the nitrogen content. In such a titration the presence of the amino groups is obscured.

No oxidation-reduction potentials with which we can confidently characterize the system were obtained because of the extreme rapidity of the potential-changes following oxidation. The system appears to be positive to that of benzidine, as is to be expected from what is known of the effects of sulfonic acid substitutions in other systems.

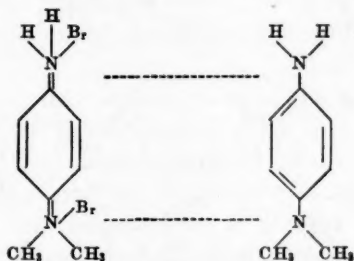
## DICHLORO-O-TOLIDINE

A preparation was made after the method of Schlenk and Knorr (1908). The very low solubility forced the use of very low concentrations which left electrode potentials wavering; and this combined with drifts of potentials prevented any results further than rough estimates that the system is positive to that of o-tolidine and somewhere near benzidine.

## WURSTER'S RED

On partial oxidation of para amino dimethyl aniline, Wurster and Sendtner (1879) obtained a remarkable material which they crystallized from alcohol and from which, by reduction, they recovered the parent compound. Willstätter and Piccard (1908), as we have already remarked, regarded this partial oxidation product, which had come to be known as Wurster's red, as a meriquinone.

The meriquinone obtained by bromine oxidation they depicted as follows:



Following the method of Willstätter and Piccard, we prepared Wurster's red in glacial acetic acid by oxidizing freshly prepared, redistilled p-amino dimethyl aniline with one equivalent of bromine.

The Wurster's red was recrystallized at once from hot, commercial "absolute" methanol with poor yield but in beautiful clear crystals. This material, when bottled, was found to keep well, as Willstätter and Piccard state.

On the assumption that Wurster's red is comparable to quinhydrone it should yield electromotive force data comparable to those of quinhydrone (Granger & Nelson, 1921, Biilmann, 1920 LaMer & Baker, 1922, Conant & Fieser, 1922).

We found, however, that no steady potentials were obtained in aqueous buffer solutions. The reason soon became evident. Some sort of transformation set in immediately when our preparations were brought into contact with water. This was very strikingly evident under the microscope.

Crystals of Wurster's red were placed between a microscope slide and a cover glass and then, under focus of a low-power objective, a drop of buffer solution was allowed to come in contact with the crystals.

With buffer of pH 1.4 the original fuchsinlike color became purple and then slowly faded to a brown. With buffer of pH 5.0 the crystals gave to the solution an initial fuchsinlike color. After about one minute, specks began to appear in the previously clear solution and finally all of the original color had disappeared, leaving a field thickly dotted with dark specks. In one instance this formation of specks took place as the crystals faded from view and left ghosts of the original crystals. In buffer of pH 7 the initial fuchsinlike color appeared as in the other cases but gave way much more quickly to specks which aggregated into flocs. In a few minutes the field of view had none of the original color but was occupied by flocs and by specks, the arrangement of which outlined some of the original crystals.

These and other experiments suggested that, if any electrode potentials significant for the initial stage in the oxidation of p-amino dimethyl aniline are to be found, they must be obtained by rapid operations, unless, perhaps, more stabilizing conditions are to be found in the use of organic solvents or by a consideration of factors to be discussed in later sections.

On operating with solutions as dilute as those used in the experiments with o-tolidine (0.0001 molar), the drifts of potential were so rapid that before a second portion of oxidant could be added in the course of a titration the product of the first addition had evidently disappeared. This, at least, is our interpretation of the experimental fact that in titrations with very dilute chlorine water the potentials drifted negatively with great rapidity and that there were required in different experiments more than two and sometimes four equivalents of the oxidant before that large positive change in potential

was reached which is ordinarily indicative of an end point. We were about to give up the attempt when a further trial was made with more concentrated solutions.

Freshly distilled p-amino dimethyl aniline, having a very slight yellow color incident to its being transferred in contact with air, was added to deaerated water. By weight there was formed a 0.015 molar solution. This had but a barely visible trace of pink color. Of this aqueous solution 10 c. c. were measured from a protected burette into 50 c. c. of deaerated buffer. The titration was then made with dilute chlorine water (approximately 0.02 normal) which had been freshly prepared and kept cold.

The concentration of the base added to the buffer was considerably higher than would be allowable in accurate measurements because it overtaxed the buffer. However, the oxidation reaction with chlorine should be such as to leave the pH value at the mid-point of the titration very near that of the original buffer solution.

In this titration a very sharp change of potential, indicative of a true end point, was observed. Assuming this and charting the experimental data in an  $E_h$ : percentage oxidation diagram we have the picture shown in Figure 2. Here the experimental data for the case mentioned, in which the pH of the buffer solution was 1.98, are shown by the centers of dots. Near these and centered by guess is drawn the theoretical titration curve for two equivalents. This experiment was duplicated with comparable results.

With an entirely different solution of the reductant and in two different buffers a second observer, operating with half the concentration used in the first instances, observed the data charted in Figure 2 by circles and crossed circles.

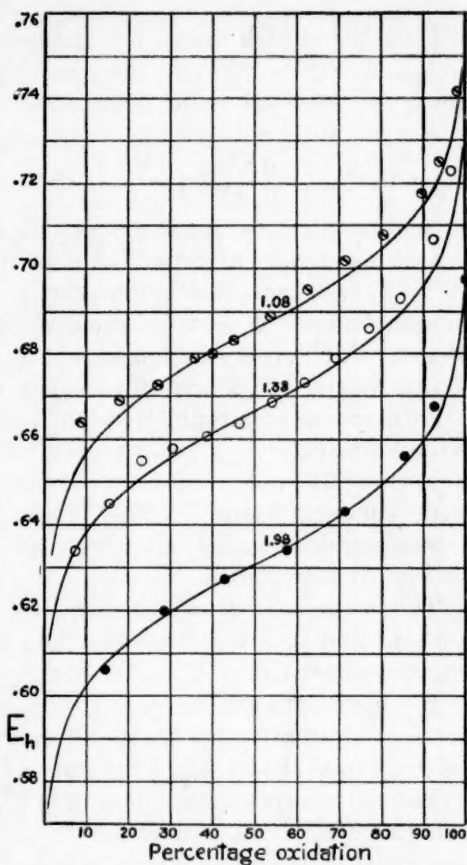


FIG. 2.—Titration curves of p-amino dimethyl aniline in buffers of indicated pH values



If it be granted that the type curves of Figure 2 have been fairly placed with reference to the experimental data, we find the following relations:

pH	$\pi_h$	$E'_o$	$E_o$
1.08	-0.065	0.686	0.751
1.38	-.083	.667	.750
1.98	-.119	.632	.751

Here  $E'_o$  in each instance is the center of the type curve placed as found in Figure 2,  $\pi_h$  is the experimentally determined hydrogen electrode potential of the buffer used, and  $E_o = E'_o - \pi_h$ .

A constant value of  $E_o$  obtained in the manner shown above indicates that  $-\frac{dE'_o}{dpH} = 0.0601$  as is found for so many organic systems in acid solution and for the o-tolidine system.

It remains then to determine the entire  $E'_o$ :pH curve.

To 50 c. c. deaerated buffer solution were added 5 c. c. of a 0.015 molar solution of p-amino dimethyl aniline prepared as described above. A chlorine solution which, in a previous titration, had been found to give a change of potential indicative of an end point at 11.00 c. c. was then rapidly added in 5.50 c. c. quantity to the buffer-reductant mixture while a stream of nitrogen rapidly stirred the mixture. The potentials used were those of the first rapidly observed potentiometric balance. These data are plotted in Figure 1. The crossed circles on the curve represent the data of the experiments previously mentioned.

The reader may draw a straight line as a "best curve" and he will perhaps find that this describes the trend of the data as well as the curve we have drawn.

We have omitted this straight "best curve" to avoid confusion with an alternative curve, the placing of which entails considerable calculation that the reader may not care to undertake.

The alternative suggestion depends upon an additional set of experimental data, namely, hydrogen electrode measurements of the course of the titration of the reductant with hydrochloric acid.

Freshly distilled p-amino dimethyl aniline was added with minimum air exposure to deaerated, double-distilled water to make a 0.015 molar solution. Forty c. c. of this were added to 20 c. c. of deaerated, double-distilled water in a vessel such as was used for the other titration (see fig. 1, paper III this series), liquid junction with the calomel half cell having previously been established in bulb S of the figure referred to by means of the solution of the base.

Two palladium-coated electrodes were used, and these were thoroughly saturated with hydrogen before the titration was begun.

Titration was done with 0.08 normal HCl solution. In a series of several titrations all in substantial agreement it was found that the two electrodes gave identical results. There were, however, indications of a long-continued and slow drift of potential. This appeared to be so like those indefinite and very slow drifts often observed with organic systems and sometimes with inorganic systems that it was decided to neglect them and to take the fairly definite potentials observed within a few minutes after each addition of hydrochloric acid.

The results of the most carefully followed titration are to be found in Tables 19 and 20.

On charting these data it was found that the first section of the titration up to one equivalent of added acid followed so closely the form of curve typical of the titration of a moderately weak base by a strong acid that there was applied directly the formula

$$\text{pH} = \text{p}K_1 - \log \frac{\%}{100 - \%},$$

treating the system simply for convenience as if mixtures of a weak acid and a strong base were being considered.

This treatment, as is evident in Table 19, yields a good value of  $\text{p}K_1$ . This  $\text{p}K_1$  is related to the basic dissociation constant by the formula  $\text{p}K_w - \text{p}K_1 = \log \frac{1}{K_b}$ .

Using Michaelis' (1914) value of  $\text{p}K_w = 13.73$  we obtain  $K_{b1} = 3.89 \times 10^{-3}$ , or  $\text{p}K_{b1} = 7.41$ .

In Table 19, calculations for the last part of the first section of the titration have been omitted for the reason that the second dissociation is coming into play.

Calculations applicable to the second section require another form of treatment because the titration curve is a resultant of the type curve applicable to moderately weak bases and the curve which Van Slyke (1922) calls the titration curve of water.

Assuming that the first section of the titration has left a salt which can be treated as a neutral salt for present purposes, we have to deal now with an equilibrium expressed by

$$\frac{[\text{B}^+][\text{K}_w]}{[\text{H}^+][\text{BOH}]} = K_{b2}.$$

Assuming complete dissociation of the chlorid formed on addition of hydrochloric acid, and by comparison negligible dissociation of BOH,  $[\text{B}^+] = [\text{added HCl}]$ . Then, also, the residual value of  $[\text{BOH}]$  will be  $C$  (total base)  $- [\text{H}^+]$ . Hence the approximation formula

$$\text{p}K_{b2} = \log \frac{[\text{H}^+](C - [\text{H}^+])}{[\text{HCl}][\text{K}_w]}.$$

The data yield, with the aid of this equation, a fairly consistent set of values for  $pK_{b_2}$  (Table 20), the average of which is 11.1, giving  $K_{b_2} = 7.94 \times 10^{-12}$ .

These approximations will be sufficient for present purposes, although for application in a precise consideration of the oxidation-reduction data the "apparent constants" should be determined for the specific salt concentration used in the oxidation-reduction measurements.

We have then for the reductant:

$$K_{b_1} = 3.89 \times 10^{-8}; pK_{b_1} = 7.41; 13.73 - pK_{b_1} = 6.32;$$

$$K_{b_2} = 7.94 \times 10^{-12}; pK_{b_2} = 11.1; 13.73 - pK_{b_2} = 2.62.$$

Returning now to the oxidation-reduction data, we have to consider the effects of dissociation of oxidant and reductant upon the  $E'_o$ : pH curve.

Without repeating the argument, we can carry over to the case at hand the theoretical equations (a) and (b), page 2 and the remarks made upon the experiments with o-tolidine. However, in the present instance the dissociation constants of the reductant, instead of being close together in value, as in the case of o-tolidine, are distinctly different, as would be expected of the difference between an amino group and a dimethyl-amino group. There is still left the theoretical possibility of determining  $pK_{o_1} + pK_{o_2}$ , but in this instance the data for neutral solutions are so uncertain that the procedure used for o-tolidine becomes even more uncertain in its present application. A guess yields  $pK_{o_1} = 7.4$  and  $pK_{o_2} = 3.7$ . With these values, with the known values of  $pK_{r_1}$ ,  $pK_{r_2}$ , and  $E_o$ , the curve for p-amino dimethyl aniline in Figure 1 was constructed.

Summarizing, we have the following constants for the p-amino dimethyl aniline system:

$$E_o = +0.751;$$

$$pK_{r_1} = 6.32, \text{ or } K_{r_1} = 4.8 \times 10^{-7}, \text{ or the first basic dissociation constant of reductant} = 3.9 \times 10^{-8};$$

$$pK_{r_2} = 2.62, \text{ or } K_{r_2} = 2.4 \times 10^{-3}, \text{ or second basic dissociation constant of reductant} = 8 \times 10^{-12};$$

$$pK_{o_1} = 7.4, \text{ or } K_{o_1} = 4 \times 10^{-8}, \text{ or first basic dissociation constant of oxidant} = 5 \times 10^{-7};$$

$$pK_{o_2} = 3.7, \text{ or } K_{o_2} = 2 \times 10^{-4}, \text{ or second basic dissociation constant of oxidant} = 9 \times 10^{-11}.$$

Of these the values of  $E_o$ ,  $pK_{o_1}$ , and  $pK_{o_2}$  are probably of the correct order of magnitude, with little more that can be said in their favor. The values of  $pK_{r_1}$  and  $pK_{r_2}$  for the conditions imposed are reliable.

In short, the experimental data, although they conform perhaps as well to a "best straight line" as to the curve drawn in Figure 1, have in support of the latter, descriptive alinement, two *independently determined* constants and a plausible argument therefrom.



## P-PHENYLENE DIAMINE

Attempts to measure the system of which p-phenylene diamine is the reductant were frustrated by the extreme instability of the system.

## WURSTER'S BLUE

Partial oxidation of tetramethyl p-phenylene diamine solutions gives a beautiful blue which has come to be known as Wurster's blue. Willstätter & Piccard (1908) regard it as a meriquinone which is not half-quinoidal like Wurster's red but variable.

We encountered complexities in the study of this system and consequently will postpone discussion to Section IV.

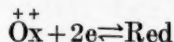
## III. Theoretical Equations

In formulating equations for the systems described in this paper we shall have to consider the occurrence of both the oxidant and the reductant in a meriquinone, M. The latter will be regarded as composed of equal parts of oxidant and reductant; and to include [M] the customary summations of the several species of oxidant and of reductant will have to be modified as in equations (1) and (2).

$$[S_r] = [M] + [\text{Red}] + [\text{H}\overset{+}{\text{R}}\text{ed}] + [\text{H}_2\overset{++}{\text{R}}\text{ed}] \quad (1)$$

$$[S_o] = [M] + [\overset{++}{\text{Ox}}] + [\text{Ox}\overset{+}{\text{OH}}] + [\text{Ox}(\text{OH})_2] \quad (2)$$

For purposes of orientation we shall assume the type structures shown by Figure 3 and that the fundamental oxidation-reduction process is



Consequently it will be convenient to formulate the ionization equilibria of the basic reductant and basic oxidant as follows:

$$\frac{[\text{Red}][\text{H}^+]}{[\text{H}\overset{+}{\text{R}}\text{ed}]} = K_{r_1} \quad (3)$$

$$\frac{[\text{H}\overset{+}{\text{R}}\text{ed}][\text{H}^+]}{[\text{H}_2\overset{++}{\text{R}}\text{ed}]} = K_{r_2} \quad (4)$$

$$\frac{[\overset{++}{\text{Ox}}][\bar{\text{O}}\text{H}]}{[\text{Ox}\overset{+}{\text{OH}}]} = \frac{[\overset{++}{\text{Ox}}]K_w}{[\text{Ox}\overset{+}{\text{OH}}][\text{H}^+]} = K'_2, \text{ and letting } K_{o_2} = \frac{K_w}{K'_2}$$

$$\frac{[\text{Ox}\overset{+}{\text{OH}}][\text{H}^+]}{[\overset{++}{\text{Ox}}]} = K_{o_2} \quad (5)$$

Likewise

$$\frac{[\text{Ox}(\text{OH})_2][\text{H}^+]}{[\text{Ox}\overset{+}{\text{OH}}]} = K_{o_1} \quad (6)$$

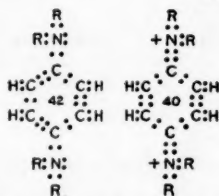


FIG. 3.—Type formulas of reductant (left) and oxidant (right)

By means of equations (3), (4), (5), and (6), equations (1) and (2) are modified to (7) and (8), wherein an abbreviation is accomplished by letting

$$x = K_{r_1}K_{r_2} + K_{r_2}[H^+] + [H^+]^2$$

$$y = K_{o_1}K_{o_2} + K_{o_2}[H^+] + [H^+]^2$$

$$[S_r] - [M] = [\text{Red}] \frac{x}{K_{r_1}K_{r_2}} = [\text{H}\ddot{\text{R}}\text{ed}] \frac{x}{K_{r_2}[H^+]} = [\text{H}_2\text{Red}] \frac{x}{[H^+]^2} \quad (7)$$

$$[S_o] - [M] = [\ddot{\text{O}}\text{x}^+] \frac{y}{[H^+]^2} = [\text{Ox}\ddot{\text{O}}\text{H}] \frac{y}{K_{o_2}[H^+]} = [\text{Ox}(\text{OH})_2] \frac{y}{K_{o_1}K_{o_2}} \quad (8)$$

Having decided to orient oxidation-reduction relations from the reaction  $\ddot{\text{O}}\text{x}^+ + 2e \rightleftharpoons \text{Red}$ , the "fundamental" electrode equation at 30° C. is

$$E_h = E - 0.03006 \log \frac{[\text{Red}]}{[\ddot{\text{O}}\text{x}^+]}$$

Hence, by (7) and (8)

$$E_h = E_o - 0.03006 \log \frac{[S_r] - [M]}{[S_o] - [M]} - 0.0601 \text{ pH} + 0.03006 \log \frac{K_{r_1}K_{r_2} + K_{r_2}[H^+] + [H^+]^2}{K_{o_1}K_{o_2} + K_{o_2}[H^+] + [H^+]^2} \quad (9)$$

When  $[H^+]$  is constant

$$E_h = E'_o - 0.03006 \log \frac{[S_r] - [M]}{[S_o] - [M]}$$

We shall show presently that, in sufficiently acid solutions and at proper concentrations of total oxidant and reductant,  $[M]$  can be made small in relation to  $[S_r]$  and to  $[S_o]$ . Then the last equation becomes (10) which is equation (a) used in the orienting experiments of Section II

$$E_h = E'_o - 0.03006 \log \frac{[S_r]}{[S_o]} \quad (10)$$

When  $[S_r] = [S_o]$ , equation (9) becomes (11).

$$E_h = E_o - 0.0601 \text{ pH} + 0.03006 \log \frac{K_{r_1}K_{r_2} + K_{r_2}[H^+] + [H^+]^2}{K_{o_1}K_{o_2} + K_{o_2}[H^+] + [H^+]^2} \quad (11)$$

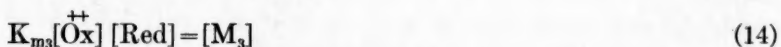
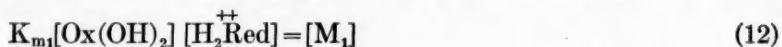
Equation (11) is the equation (b) mentioned in the previous section. By its application the dissociation constants are determined, those of the reductant being confirmed by hydrogen-electrode measurements.

The conditions of (10) and (11) are those which we tried to approximate in Section II in the experiments which were designed to outline the main characteristics of each system. In conducting

several of these earlier experiments, we were not aware of the implications in certain equations still to be developed, and, therefore, we either did not know how adequately to meet the conditions of (10) and (11) or else we were over-confident of what was believed to be a sufficient approximation to these conditions. It is, therefore, probable that a repetition of our orienting experiments under conditions the basis of which we shall presently outline will appreciably improve our data.

Before taking the next step in the theoretical treatment, two important items are to be considered:

First, Willstätter and Piccard were careful to state that a meriquinone need not be composed of equal parts of oxidant and reductant. Indeed they give instances where the evidence indicates ratios of oxidant and reductant other than unity. Now it would very seriously complicate our equations to take account of all possibilities; but, on the other hand, certain important features can be developed for the case in which the meriquinone has one, another, or all of the compositions implied in the following equilibrium equations where  $K_{m_1}$ ,  $K_{m_2}$ , and  $K_{m_3}$  are *association* constants:



What is true for such a system should serve as a prototype of relations among more complicated systems.

We limit the possible compositions to those implied in (12) to (14) for two reasons: First, the products isolated in syntheses of meriquinones of the type now under consideration are frequently salts with two acid radicles. Second, our own experiments, although difficult to interpret because of very rapid decompositions of the meriquinones in neutral and alkaline solutions, suggest that the meriquinones disappear not only in acid but also in neutral and alkaline solution as they should if the composition is one, another, or all of those implied in (12) to (14). We see but one other possibility as an explanation of the latter phenomenon. That is that the meriquinone is an intermediate ion of the oxidant. But in this case the isolated salt would be univalent and the maximum color would not be found at the pH value observed.

The second matter to be discussed is our neglect of possible ionizations of basic groups appearing in the meriquinone complex itself as distinct from the ionization of these same groups as they appear in the constituents. Here again it would seriously complicate the equations to take account of this possibility. Perhaps the dissocia-

tion constants found by inflections of  $E'_o$ : pH curves are not those of the reductant and the oxidant as assumed in Section II where the constants of the reductant were determined by hydrogen electrode measurements. Perhaps they are the resultant of the ionization of constituents of the meriquinone and of the meriquinone itself. If so the fairly close correspondence between values found by inflections of the  $E'_o$ : pH curves and values for the reductant found by hydrogen electrode measurements will be for the present sufficient justification for proceeding with the simplifying assumption that the gross aspects will not be seriously altered by neglecting the ionizations discussed. This assumption should, however, be given careful attention when the subject is again studied with refined measurements.

Proceeding, then, with the assumptions outlined above, we combine equations (7) and (8) with (12), (13), and (14) in turn to obtain the *choices* in (15):

$$([S_r] - [M])([S_o] - [M]) = \frac{[M_1]}{K_{m1}K_{o1}K_{o2}}w = \frac{[M_2]}{K_{m2}K_{r2}K_{o2}}w = \frac{[M_3]}{K_{m3}K_{r1}K_{r2}}w \quad (15)$$

$$\text{where } w = \frac{xy}{[H^+]^2}$$

It is implicit in equations (12) to (14) and (3) to (6) that  $M_1$ ,  $M_2$ , and  $M_3$  are tautomers. Which of these predominates depends upon relative values of  $K_{m1}$ ,  $K_{m2}$ , and  $K_{m3}$  the determination of which would be extremely complicated. It will presently be shown that the sum  $[M_1] + [M_2] + [M_3] = [M]$  can be determined, and therefore the equations should be modified to replace  $[M_1]$ ,  $[M_2]$ , and  $[M_3]$  by  $[M]$ .

The sum of the tautomers can be found from (12), (13), and (14). Then by the introduction of (3), (4), (5), and (6) there is obtained (16).

$$\left. \begin{aligned} [M] &= [M_1] + [M_2] + [M_3] = [Ox(OH)_2] [H_2\overset{++}{Red}] K_{m1} \\ &= [OxOH] [H\overset{+}{Red}] K_{m2} \\ &= [Ox] [Red] K_{m3} \end{aligned} \right\} \quad (16)$$

In (16)

$$K_{m1} = K_{m1} + K_{m2} \frac{K_{r2}}{K_{o1}} + K_{m3} \frac{K_{r1}K_{r2}}{K_{o1}K_{o2}} \quad (16a)$$

$$K_{m2} = K_{m1} \frac{K_{o1}}{K_{r2}} + K_{m2} + K_{m3} \frac{K_{r1}}{K_{o2}} \quad (16b)$$

$$K_{m3} = K_{m1} \frac{K_{o1}K_{o2}}{K_{r1}K_{r2}} + K_{m2} \frac{K_{o2}}{K_{r1}} + K_{m3} \quad (16c)$$

Multiplying successive equivalents in (16)

$$[M]^3 = [Ox] [OxOH] [Ox(OH)_2] [Red] [H\overset{+}{Red}] [H_2\overset{++}{Red}] K_M \quad (17)$$

where  $K_M = K_{m1}K_{m2}K_{m3}$

If [O] represents the geometrical mean of the concentrations of uncombined oxidants and [R] the geometrical mean of concentrations of uncombined reductants, then

$$[O][R]\sqrt[3]{K_M} = [M] \quad (18)$$

From (17) and still general, successive choices in (7) and (8)

$$\frac{([S_r] - [M])([S_o] - [M])}{[M]} = \frac{xy}{[H^+]^2} \sqrt[3]{\frac{1}{K_{r1}K_{o1}K_{r2}^2K_{o2}^3K_M}} = wK' \quad (19)$$

Hence

$$[M] = \frac{[S_r] + [S_o] + wK'}{2} \pm \frac{1}{2} \sqrt{([S_r] + [S_o] + wK')^2 - 4[S_r][S_o]} \quad (20)$$

In (20) only the negative sign before the root sign is significant.

If (19) is compared with the choices in (15), it becomes evident that whether the meriquinone has one, another, or all of the compositions implied in (12) to (14), its variation with alteration of  $[H^+]$  will follow the same course. For instance, all would reach a maximum at the same pH determined by the values of the basic dissociation constants. Furthermore, equation (19), which is descriptive of the more general case, makes it evident that an arbitrary assumption of one choice in (15) might lead to wrong conclusions regarding the relative proportions of different forms of meriquinone. For if (as we shall show is possible) a constant such as  $K_M$  of (19) is determinable, the relation  $K_{M1}K_{M2}K_{M3} = K_M$  and equations (16a) to (16c) reveal  $K_M$  to involve  $K_{M1}$ ,  $K_{M2}$ , and  $K_{M3}$ —all three association constants of the three tautomers, for the evaluation of which we have insufficient latitude in the variation of experimental conditions and consequently an insufficient number of applicable equations.

In short, the methods used do not permit a decision regarding the relative proportions of the species specified although they would provide data for calculating the relative proportions of constituents at any pH value, if these constituents were not withdrawn to form a meriquinone.

The value of  $K_M$  in equations (17) and (19) is a measure of the tendency of the total meriquinone to associate from all its constituents. It would be, for instance, the  $K_{M2}$  of (13) were the meriquinone constituted exclusively as implied in (13).

Since  $K_M$  of (17) equals the product  $K_{M1}K_{M2}K_{M3}$ , it might be imagined that its value is not expressive of the true tendency for association because one of the terms in the product can be imagined to approach 0 or  $\infty$ . However, equations (16a) to (16c) show that if one tautomer predominates, making the association constants of the

others approach zero,  $\sqrt[3]{K_M}$  approaches the association constant of the predominant tautomer. Thus, if but one tautomer occurs and

that is  $M_2$ , then,  $\sqrt[3]{K_M} = K_{m_2} \sqrt[3]{\frac{K_{r_2} K_2}{K_{o_1} K_{r_1}}}$ .

$\sqrt[3]{K_M}$  when evaluated furnishes an estimate of the force determining association and should be interesting because of the puzzling problem of what determines the formation of these peculiar compounds, irrespective of conditions determining the formation of the constituent ions.

An evaluation of  $K_M$  in any specific system is important if orienting data such as are described in Section II are to be extended to various applications of these meriquinones. This will be shown in more detail in a subsequent section.

$K_M$  can be evaluated as follows: Consider two cases in each of which  $[H^+]$  shall have the same value and shall be such that there would tend to be maintained appreciable quantities of the meriquinone's constituents. Let the one case be that of  $[S_r] = [S_o]$ , whence, by an abbreviation of (11),

$$E_{h_1} = E_o + 0.03006 \log \frac{x}{y[H^+]^2} \quad (11a)$$

Let the other case be one in which oxidation has proceeded to such a slight extent that the resulting value of  $[M]$  is negligible compared with the value of  $[S_r]$ . Then, by (9),

$$E_{h_2} = E_o - 0.03006 \log \frac{[S_r]}{[S_o] - [M]} + 0.03006 \log \frac{x}{y[H^+]^2} \quad (21)$$

From (11a) above and (21),

$$E_{h_1} - E_{h_2} = 0.03006 \log \frac{[S_r]}{[S_o] - [M]} \quad (22)$$

Applying the same approximation to (19) and substituting the result in (22) we arrive at (23), where  $K' = \sqrt[3]{\frac{1}{K_{r_1} K_{o_1} K_{r_2}^2 K_{o_2}^2 K_M}}$ .

$$E_{h_1} - E_{h_2} - 0.03006 \log \frac{[S_r]}{[S_o]} = 0.03006 \log \frac{[S_r] + wK'}{wK'} \quad (23)$$

That is, use is made of a new set of experimental data, namely, the deviation  $\left(E_{h_1} - E_{h_2} - 0.03006 \log \frac{[S_r]}{[S_o]}\right)$  of potentials at slight percentage oxidation from those calculated on the assumption of no appreciable association of constituents to form a meriquinone. Consequently, since other components of (19) are known,  $K_M$  is determinable.





Whence,

$$E_{h1} - E_{h2} = 0.03006 \log \frac{[S_r]}{[S_o] - [M]}$$

[M] being thus determined, it follows from (B), (C), and (D) that  $K_M$ , the dissociation constant of the meriquinone, is determined.

Thus all the terms of the general equation (A) as well as  $K_M$  of (D) are found experimentally through actual effects upon electrode potential, or, in other words, the final equations contain no constant or variable not subject to experimental verification.

Equation (A) describes a surface which *in outline* has three dimensions:  $E_h$ , pH, and percentage oxidation. It has the general character of Figure 2 of the sixth paper of this series, but it has a more uniform over-all slope. The unique character is a widening along any line of constant pH where pH permits the formation of a meriquinone. This picture is incomplete, however, because it does not include the effects of changes in concentrations as revealed in equation (B).

A very remarkable theoretical consequence of the manner in which the total concentration of the system occurs in equation (B) will be discussed in connection with our remarks on the tetra methyl p-phenylene diamine system, page 34.

#### IV. Completing Data

The equations developed in Section III show that the outline data of Section II are insufficient to describe the peculiar systems which are under discussion. We shall now give the completing data which are required for numerical solution of the complete equation.

It will be remembered that the instability of the partially oxidized solutions prevented precise electrode measurements and left a considerable degree of uncertainty in the values of several constants, notably,  $K_{o1}$  and  $K_{o2}$ , described in Section II. These uncertain values have to be carried over into the following discussion and consequently a high order of agreement between the predictions of the new equations and the experimental data is not to be expected.

In Tables 21 and 22 are data for the calculation of the dissociation constants of the meriquinone of tolidine and of Wurster's red, and also for the concentrations, [M], in each case for the dilution used. The data were obtained as follows:

A measured amount of a known solution of the reductant was added to each of several deaerated buffer solutions. To each mixture was added the same amount of standardized chlorine-water so as to induce a small but definite percentage oxidation. These controlled conditions give the actual values of  $[S_r]$  and  $[S_o]$ . The pH values of the mixtures we assume to be those of the diluted buffers as measured with the hydrogen electrode. The potentials,  $E'_o$ , of the stage of 50 per cent oxidation were calculated from the data of Section II.



Were no meriquinone formed, the difference  $E'_{\text{o}} - E_{\text{h}_2}$  should be constant at any value of pH. The observed variation in this difference within the pH region of meriquinone formation permits the calculation of  $[M]$  in each instance by equation (22) or of  $K'$  by equation (23).

In the case of the meriquinone of o-tolidine there is a distinct trend in the values of  $K'$  (Table 21). Nevertheless within the range of pH where the method is best applied, the order of magnitude remains the same. The average 550 for  $K'$  yields  $\sqrt[3]{K_M} = 1.5 \times 10^6$  from 
$$K_M = \frac{1}{(K')^3 K_{r1} (K_{r2})^2 K_{o1} (K_{o2})^2}$$

In the case of Wurster's red (Table 22) there is no distinctive trend in the values for  $K'$  and a much better agreement.

For purposes of comparison we may use the values of  $\sqrt[3]{K_M}$ , which are  $1.5 \times 10^6$  for the o-tolidine meriquinone and  $1.1 \times 10^6$  for Wurster's red. Both are of an order of magnitude which indicates a very great tendency for the meriquinones to form from their constituents when the reaction of the solution permits the formation of the constituents. This magnitude indirectly indicates considerable intensity in the forces which determine the association. It is very large in comparison with the value 3.8, which is approximately that found by Sørensen, Sørensen and Linderstrøm-Lang (1921) for quinhydrone's association constant.

While the particular values used in drawing this conclusion depend, as we have emphasized, upon somewhat dubious values for several constants, the general import of the conclusion is not thereby seriously affected, for it can be discerned in the original experimental data.

The value of  $\sqrt[3]{K_M}$  in the case of Wurster's red is about 667 times that of the o-tolidine meriquinone. This difference, as well as the individual effects of meriquinone association, should be evident in the effects of various conditions upon colors; for, having determined by potentiometric methods at least the orders of magnitude of the constants which characterize the tendency for meriquinone-formation, and having specified in particular instances the actual concentrations of meriquinone, it should be possible to calculate percentages of maximum color in specific instances and to determine how far the predictions are confirmed by actual experiment.

Before discussing such experiments we shall mention a study of the absorption spectra.

#### ABSORPTION SPECTRA

Investigation of absorption spectra of solutions comparable with those with which we are now dealing has been confined, with few exceptions, to the study of quinhydrone solutions. It is evident in

the many investigations of quinone-quinol systems that the absorption is not of the type of the meriquinones. This is evidently due to the comparatively negligible association of the constituents of quinhydrone in aqueous solution. See for example, Hartley (1902), Baly and Stewart (1906), Schlenk (1909), Pfeiffer (1914, 1917), Lifschitz (1916, 1917), Lifschitz and Jenner (1915), and Klingstedt (1923). Many addition compounds of the general type of phenoquinone, of quinone in combination with other substances, of trinitrobenzene in many combinations, as well as a variety of other combinations, have been studied, but seldom by other than chemical methods. See Pratt and Gibbs (1913), Hantzsch (1916), Sudborough (1916).

Sudborough states that while the hydroxy-, alkyloxy-, and alkyl-amino-groups in the additive compounds act mainly as auxochromes, they also tend to increase the stability of the compounds. Hantzsch (1917) concludes from his study of the effects of solvent on solute that the general nature of the absorption is not affected to any great extent by the formation of molecular compounds, whether the compounds are alike or unlike, provided the process is not accompanied by a change in molecular constitution.

In cases where the potentiometric method is applicable, it should enable investigators to determine the specific influences of auxochrome groups upon dissociations of constituents as well as upon the associative tendencies of the quinhydrone-like complexes.

An investigation of color in the systems under discussion was made with a Keuffel and Esser "color analyzer," the scale readings of which are percentages of transmission at indicated wave lengths.

Since we had to deal with solutions the colors of which were subject to rapid changes, a special cell 10 cm. long was constructed for rapid filling. It had permanent end plates and a side tube large enough to allow the solution to be poured in rapidly. An ordinary 1 cm. tube requiring more time to fill was used in a few instances.

These limitations in tube length necessitated adjustments of conditions until color of about the same order of magnitude was produced, and consequently not only restricted the range of conditions which could be studied in an effort to determine whether or not the equations could be confirmed, but also left the experimental errors large in relation to the variations in color that were found.

In addition to the fading which occurs in all the meriquinone solutions examined, there is an enhancement of color which occurs during the irradiation of solutions of p-amino dimethylaniline and of tetramethyl p-phenylenediamine. (Compare with our findings in the case of methylene white, Paper No. 8, this series). These opposite effects of fading and enhancement of color probably seldom balance while the solutions are being examined in the spectrophotometer. Furthermore, air can slowly oxidize reductants of the p-phenylene diamine

series. The only provision to reduce the latter error was the de-aeration of the buffer solutions. Of course, the stock solutions of reductants were preserved under nitrogen, but the mixtures were exposed during the few minutes of observation.

These several sources of error were recognized. Accordingly, every effort was made to operate rapidly and to confirm important characteristics of the absorption curves. Thus, while it may appear

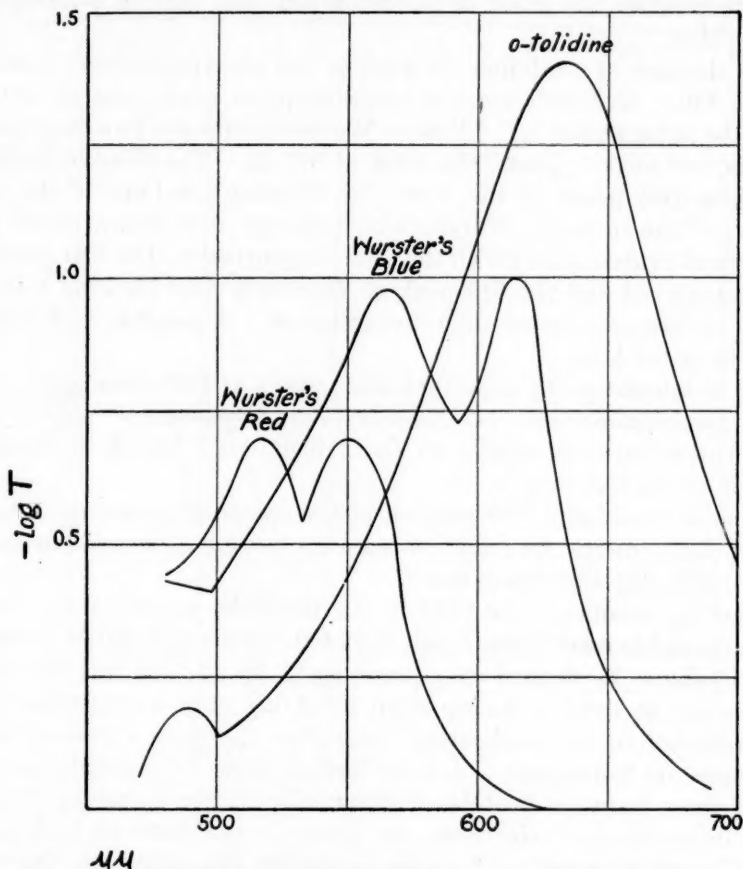


FIG. 4.—Absorption curves of meriquinones of o-tolidine, of tetramethyl p-phenylene diamine (Wurster's blue), and of p-amino dimethyl aniline (Wurster's red). (Relative heights have no general significance in these comparisons)

in the citation of a single experiment as if a peak in an absorption curve were determined by only one reading, the position of this peak was fixed by approach from both sides in repeated experiments.

For purposes of comparing the positions of peaks only, there are shown in Figure 4 typical absorption curves for partially oxidized solutions of p-amino dimethyl aniline, tetramethyl p-phenylene diamine, and o-tolidine. The conditions were as follows:

p-Amino dimethyl aniline: 30 per cent oxidation of a  $3.28 \times 10^{-5}$  molar solution at pH 2.9. 10 cm. tube.

Tetramethyl p-phenylene diamine: 50 per cent oxidation of a  $1.1 \times 10^{-5}$  molar solution at pH 3.8. 10 cm. tube.

o-Tolidine: 3 per cent oxidation of a  $1.97 \times 10^{-4}$  molar solution at pH 3.8. 10 cm. tube.

It is evident from these curves that the meriquinone of p-amino dimethyl aniline, Wurster's red, gives a red solution, that of tetramethyl p-phenylene diamine, Wurster's blue, a blue with sufficient red to produce the effect of dichromatism, and that of o-tolidine a purer blue.

In the case of o-tolidine the peak of the absorption curve centers at  $\mu\mu$  630. Wurster's red has two absorption peaks, one at 520  $\mu\mu$  and the other at 550  $\mu\mu$ . Likewise Wurster's blue has two absorption peaks, one at 565  $\mu\mu$  and the other at 615  $\mu\mu$ . The relative heights of these two peaks of the curve for Wurster's red and of the two peaks of the curve for Wurster's blue change with alteration of the degree of oxidation and with the total concentration, the 550 peak of Wurster's red and the 615 peak of Wurster's blue showing a tendency to disappear under some circumstances. A possible explanation will be noted later.

It is interesting to note that Hantzsch's (1916) investigation of the meriquinone salt of N-methyl-dihydrophenazine shows two absorption maxima similar to those just noted, but in a different region of the spectrum.

Before considering the relation of the spectrophotometric data to the potentiometric we might note an interesting aspect of our mode of formulating a meriquinone.

Having insufficient latitude in our methods, we could not determine possible association constants of the three postulated forms of meriquinone as defined in equations 12 to 14. It was therefore necessary to develop an equation involving only a single constant of association, the implication being that the three forms of meriquinone are tautomeric. A little further inspection reveals the fact that these forms as postulated differ only in two respects. One is the distribution of electrons, the other is the state of hydration. The latter is merely a formalistic matter depending on the convenient method of formulation adopted. The first may be regarded as in harmony with what we understand to be Stieglitz's (1924) theory of the cause of color in compounds of this type, namely, a structurally oxidized and a structurally reduced position in the molecule permitting directly or indirectly wide latitude in the electron oscillations. The justification of this theory must of course ultimately depend upon quantitative rather than qualitative evidence. Potentiometric data on the effects of substitution, their aid in resolving certain outstanding difficulties connected with the high color of completely oxidized diamines, and particularly their contribution to

the resolution of the state of the constituents from the state of the associated product should prove to be valuable.

#### O-TOLIDINE

In Table 23 are shown the experimental data found when o-tolidine solutions of the indicated concentrations were oxidized to different degrees.

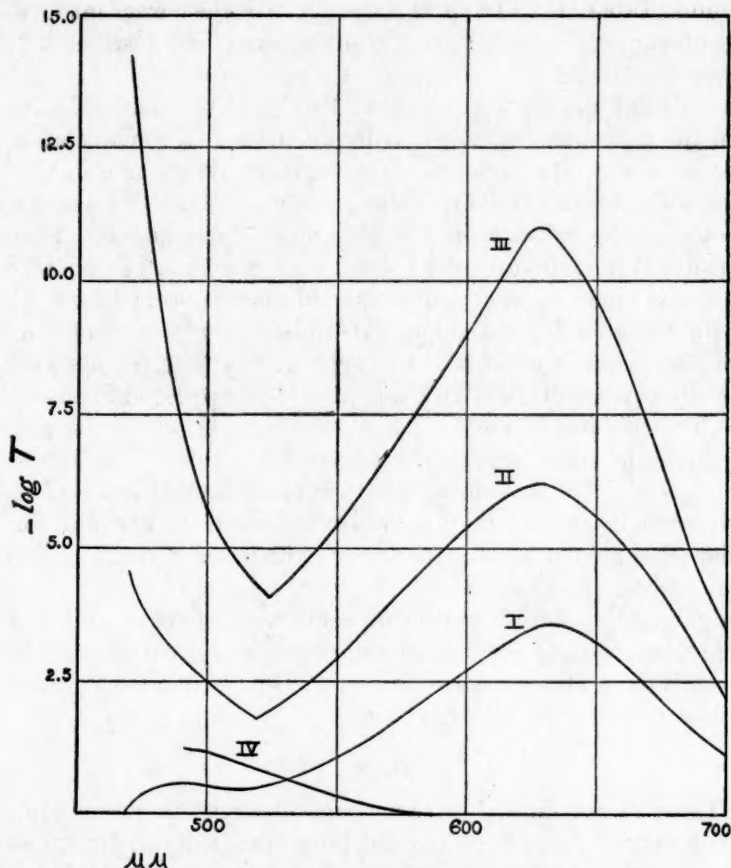


FIG. 5.—Absorption curves for three cases of partially oxidized solutions of o-tolidine when absorptions are reduced to a common basis of  $10^{-5}$  molar meriquinone in 10 cm. Curve IV is a special case of the absorption by a fully oxidized solution

Since the several constants and the equation determining the extent of the formation of the meriquinone are supposed to be known, it should be possible to calculate  $[M]$  for each of these cases and then to reduce the values of  $-\log T$  to the common basis of  $10^{-5}$  molar meriquinone in a 10-centimeter tube. The results of these calculations are exhibited in Table 23. The corresponding curves are shown in Figure 5.



Were the basis of calculation correct and the constants used accurate, the absorption peaks at  $\mu\mu$  630 should now coincide. That they do not, and that the reduction of the data to a common assumed basis has only produced an inadequate degree of approach is good evidence of error in the basis of calculation, in the values of the constants used, or in the immediate experiments. Of the constants used,  $K'$  is the least accurately known. Changing its value from the 550 found (Table 21) to 100 brings the peaks of the curves into reasonable conformity; but so arbitrary a procedure is not justified.

However, certain other relations are now revealed.

The calculations shown in Table 23 indicate a considerable variation in the concentration of the holoquinone which remains after the formation of the meriquinone. It is comparatively small in the case illustrated by curve I (fig. 5). Therefore, curve I may be assumed to characterize the absorption by the pure meriquinone. There is absorption in the red and yellow, less in the green, and comparatively little in the blue. Consequently the solution appears blue. Curve IV is for the holoquinone alone. Its chief absorption is in the blue end of the visible spectrum. Consequently, if our calculations are essentially correct (Table 23), there should be appreciable absorption of the blue in Case II and still more in Case III where the residual holoquinone is quite large. The curves show this. The subjective color is green. Thus, even though our formulations fail to describe the situation with accuracy they are sufficient to account for the peculiar changes from blue to green which occur with change of circumstances.

Roughly, also, the alteration of color with changes in pH, total concentration, etc., as predicted by the equations, are confirmed by the color analysis. These other relations will be discussed when we have described the data for Wurster's red.

#### WURSTER'S RED

In Table 24 are shown the experimental observations for solutions buffered at pH 3.8. For the conditions specified and by the use of constants evaluated potentiometrically there were calculated the concentrations of meriquinone and of residual holoquinone in each case as shown in the table. This permitted the reduction of the spectrophotometric data to a common basis of  $10^{-5}$  molar meriquinone in a 10 centimeter tube as was done for the tolidine data. The resulting absorption curves are charted in Figure 6.

In this case the tendency to conformity is much more distinct. However, we now encounter a peculiarity for which we are unable to account. The completely oxidized solution shows an absorption (curve IV) of the same type as the supposed meriquinone. Were it that of a true holoquinone the data for the meriquinone before being

reduced to the common basis should be corrected for absorption by those concentrations of holoquinone exhibited in Table 24. If this be done it is found not seriously to alter the relations; but we would not feel justified in making such a correction till the absorption at 100 per cent oxidation is definitely proved to be that of a true holoquinone. Incidentally, we might note that both in the case of Wurster's red and in the case of Wurster's blue the two peaks of the absorption curves are altered in their relative heights by change of conditions in much the same way that they would be were the true meriquinone curves superimposed upon the "holoquinone" absorption curves of Type IV, Figure 6.

However, it is evident that we are encountering a situation which is as yet too difficult to analyze with a clarity sufficient for present purposes. On the other hand, it should be possible, by taking the difficulties into consideration, and by restricting experiments to conditions where all variables but one are fixed, to show certain relations in rough outline.

To demonstrate the effects of alteration of pH upon color when total concentration and percentage oxidation are kept constant we used colorimetric readings.

In Figure 7 there is shown by curve A the variation in percentage of maximum color with variation in pH which would occur were the Wurster's red but an extremely small fraction of the concentrations of the constituent species. This would be the condition that the association constant approaches zero or that  $K'$  approaches infinity. In curve B there has been applied in equation 20, page 21, the value  $5.6 \times 10^{-1}$  for  $K'$ , the other conditions being  $[S_r] = 2.95 \times 10^{-5}$  and  $[S_o] = 2.72 \times 10^{-5}$ . For these conditions the experimental values shown by circles were found. Curve C was calculated with the same value of  $K'$  and for the conditions  $[S_r] = 4.04 \times 10^{-4}$ ,  $[S_o] = 1.0 \times 10^{-5}$ . The experimental values for this last set of conditions are shown by blackened circles. To illustrate the calculations used in these and several other cases there is given in Table 25 the procedure used for curve C.

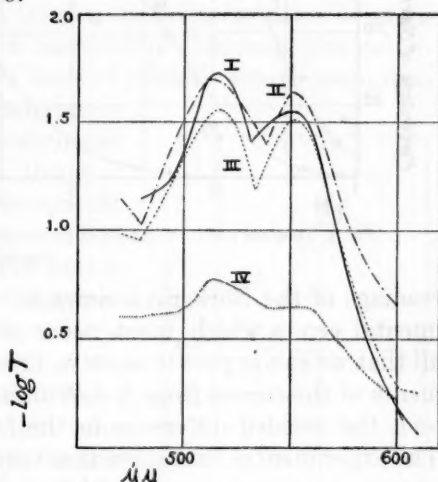


FIG. 6.—Absorption curves for three cases of partially oxidized solutions of p-amino dimethyl aniline when absorptions are reduced to a common basis of  $10^{-5}$  molar meriquinone in 10 cm. Curve IV is a special case of the absorption by a fully oxidized solution

Since the color of these solutions fades rapidly it was impracticable to set up a colorimetric standard of Wurster's red. There was used a more permanent standard composed of an empirical mixture of acidified methyl red and thymol blue. Furthermore, the fading of the solutions under test was so rapid that graphic extrapolation to zero time had to be made from a large number of rapidly made

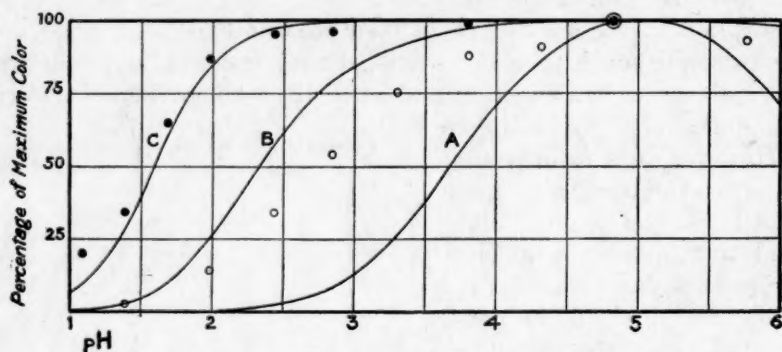


FIG. 7.—Wurster's red. Variation of percentage maximum color with variation of pH.  
(See text)

readings of the Bürker colorimeter. In view of the inevitable experimental errors which must occur under such circumstances, about all that we can expect to show is, first, the very considerable displacements of the curves from A due to meriquinone association and, second, the decided difference in the form of curve for the two cases. The experimental data show these aspects. Otherwise the agreement

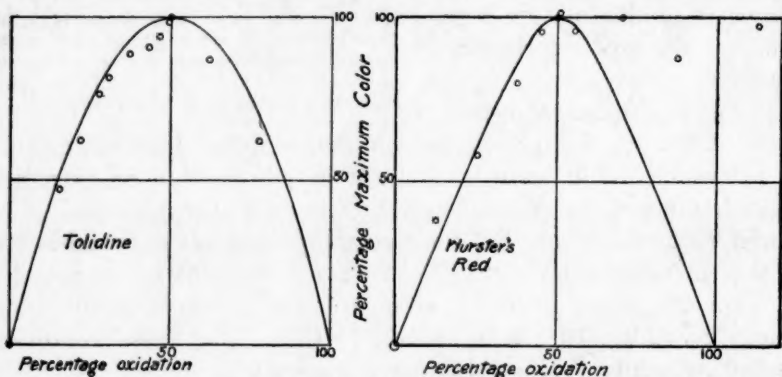


FIG. 8.—Comparison of the percentages of maximum color at various stages of oxidation in the case of o-toluidine with the case of p-amino dimethyl aniline

is unsatisfactory. A similar picture is obtained with the toluidine system; but in this case the displacement is comparatively slight, as is to be predicted from the relatively smaller value of the association constant.

Another way of showing the difference in the orders of magnitude of the association constants of Wurster's red and of the meriquinone



of o-tolidine is in the comparison of the curves relating percentages of oxidation and percentages of maximum color. In the cases illustrated by Figure 8, pH was constant. The percentages of maximum color were measured in these instances by the relative heights of absorption peaks. The curves which are shown in these two figures of Figure 8 were charted from calculations. There is evident a rough conformity up to 50 per cent oxidation. From then on the Wurster's red system shows the peculiarity previously mentioned. However, the point to be noted is the greater curvature of the tolidine relations between 0 and 50 per cent due to the lower association.

If now use is made of the calculated actual concentration of meriquinone in one case to serve as a standard of reference, the colorimetric data can be reduced to the basis of relative actual concentration instead of the percentages of maximum illustrated in Figure 8. The recalculated data are exhibited in Figure 9, together with the curves calculated for these specific cases.

Figure 9, while it does not serve better than Figure 8 to show experimental agreements and discrepancies, does show very clearly several important features.

It makes it graphically evident that Wurster's red has such a high association constant that in this instance it forms to the extent of 80 per cent of the limit available (indicated by W's) at 50 per cent oxidation. On the other hand the meriquinone of the tolidine system in the comparable case forms to the extent of only 8 per cent of the limit available (indicated by T's). One consequence, which can be shown more perfectly by use of the complete equations, is that under the most favorable conditions of pH, total concentration, etc., it is impossible to develop the meriquinone color of the tolidine system to the extent that is possible in the p-amino dimethyl aniline system. It is only by comparing light absorptions for comparable concentrations of the two meriquinones themselves that the greater absorption by the tolidine meriquinone at its maximum is revealed.

Figure 9 will perhaps serve better than the complete equations to make evident a matter of considerable importance to future investi-

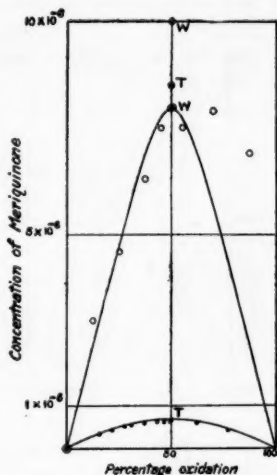


FIG. 9.—Variations in the concentrations of the meriquinones of o-tolidine and of p-amino dimethyl aniline with variation in percentage oxidation in two specific and comparable cases. (Figure 8 recalculated to a new basis)

gations. In the case of Wurster's red the withdrawal of constituents to form meriquinone can be so extensive as to make potentiometric measurements precarious. Thereby errors are introduced into the fundamental data. In the case of the tolidine system the withdrawal may not so seriously affect the fundamental electrode data, but, by the same token, the effects of meriquinone formation are not so strikingly evident either upon the potential deviations which are used to determine the meriquinone association constant or upon certain colorimetric observations. Thus it is evident that a precise alignment of colorimetric and potentiometric measurements will require of each method the utmost accuracy.

#### WURSTER'S BLUE

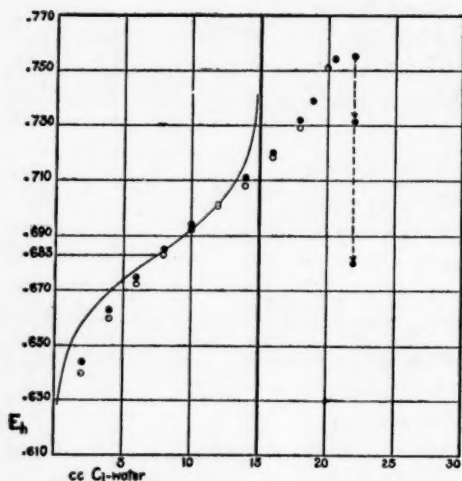


FIG. 10.—Graphic representation of duplicate attempts to determine a titration curve for tetramethyl p-phenylene diamine

We have already mentioned the fact that drifts of potential were so rapid that we obtained no accurate and no satisfactory data for the system of tetramethyl p-phenylene diamine, the meriquinone of which is known as Wurster's blue. We shall, therefore, merely cite our data and shall utilize it, not as the occasion to attempt any definition of the system, but as the occasion to discuss a most interesting prediction found in the equations.

Titration of an unanalyzed sample of tetramethyl p-phenylene diamine from the Eastman Laboratories gave titration curves of which Figure 10 is a representative example. The pH value of the buffer solution was 1.08. The reductant was 0.001 molar, and the chlorine water 0.0069 normal. Hence there should have been evidence of a "break" in the curve when 15 c. c. of oxidant had been added. However, this may have been obscured by the drift of potential, which, at this point, had become so rapid that the greatest haste was necessary to preserve any semblance to the ordinary titration curve. When 22 c. c. had been added, the drift was followed. The potential dropped to 0.731 in the first 3 minutes and to 0.680 in the subsequent 30 minutes. Simply to fix upon an  $E'_0$  value which can be compared with other data, we guess 0.683 by methods made plain in the construction of the figure.

Let us now study the data for the  $E'_0$ :pH curve. For purposes of comparison there are shown in Figure 11 the  $E'_0$ :pH curve (A) of Wurster's red and the companion curve (B) calculated for 2.6 per cent oxidation of a  $2.7 \times 10^{-4}$  molar solution of p-amino dimethyl aniline. The extent to which (B) departs from parallelism with (A) is indicative of the magnitude of the meriquinone association constant.

The blackened circles of Figure 11 represent the more consistent of two sets of unsatisfactory data found in an attempt to determine the  $E'_0$ :pH curve for the Wurster's blue system. The position of the cross is taken from Figure 10. The conclusion which follows and which is presented only for its theoretical interest is based on a somewhat circular argument in which it is assumed that the experimental data are in error, for a reason which will presently be plain, and that the true curve roughly parallels that of the Wurster's red system.

The fairly reliable data for the Wurster's blue system at 2.6 per cent oxidation of  $2.7 \times 10^{-4}$  molar tetramethyl p-phenylene diamine are shown by circles in Figure 11. If the above assumption be granted for the sake of the argument, the appreciably greater deviations in the case of the tetra system may be taken as evidence of a higher value for the association constant. This would account for the formation of the blue color at low pH values in spite of the fact that we would expect an enhancement of basic dissociation by the introduction of methyl groups and consequently a shift of the zone of meriquinone formation toward higher pH values.

Now a marked increase in the value of the association constant would produce the peculiar effect which we wish to note. The effect can be illustrated by calculations for hypothetical cases in which the constants for Wurster's red are used. In Figure 12 are shown the calculated curves relating potential to percentage oxidation at pH values indicated and for a low total concentration of material ( $10^{-5}$  M), set A, and a high concentration of material ( $10^{-1}$  M), set B. For purposes of comparison, these curves are given a common center, and only the first half of each symmetrical curve is illustrated.

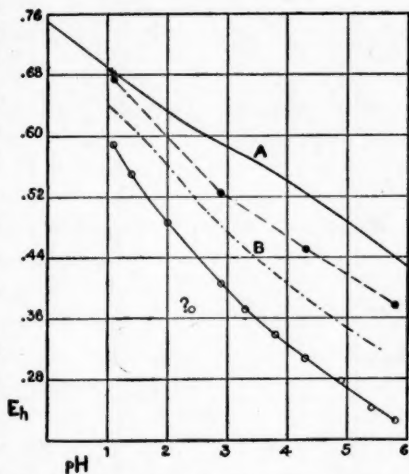


FIG. 11.—Comparison of  $E'_0$ :pH curve (A) of p-amino dimethyl aniline system and of the corresponding  $E_h$ :pH curve at 2.6 per cent oxidation of a  $2.7 \times 10^{-4}$  molar solution (B) with the corresponding experimental curves of the tetramethyl p-phenylene diamine system

At low concentration and at low pH so little meriquinone is formed that the curve approaches the normal. Increase of pH causes the curve to deviate from the normal until the maximum deviation is attained at pH 5 in this system. These deviations are very greatly accentuated by increasing the total concentration, so that when the concentration reaches tenth molar there is a distinct separation of two portions of the curve, as illustrated by the B set of curves. It will be remembered that we are illustrating only the section from 1 to 50 per cent oxidation. This separation occurs because, in the one

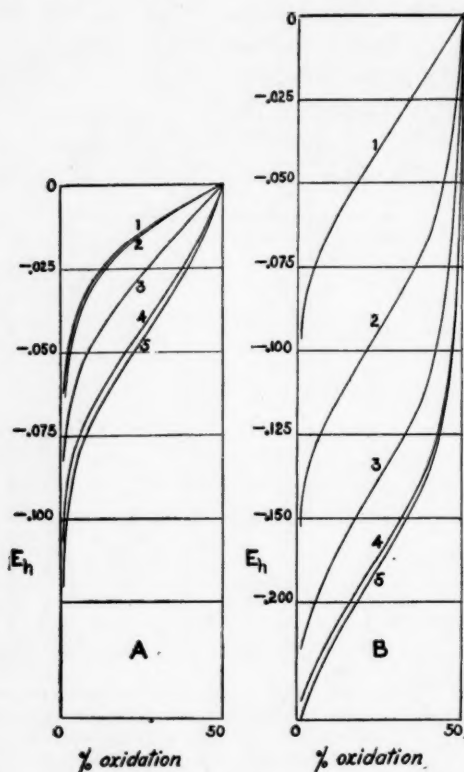


FIG. 12.—First half sections of  $E_h$ : Per cent oxidation curves calculated with the constants of the Wurster's red system to show theoretically the effects of pH (as indicated) at low total concentration (A) and at high total concentration (B)

evident that potentials of the half oxidized system should be unstable in the region of meriquinone formation independent of any drifts due to decomposition of components of the system.

If this deduction were to be confirmed by more accurate measurements than we have been able to obtain, and were it applicable in

the high concentration of reductant has absorbed practically the entire amount of oxidant and, in the other instance, the oxidant has absorbed practically the entire amount of reductant to form meriquinone; and the system behaves as if there were two virtually distinct oxidation-reduction systems, the first being meriquinone and excess reductant and the second meriquinone and excess oxidant. Of particular interest is the absence of poisoning action at 50 per cent oxidation, where ordinarily the greatest poisoning action occurs.

Now this theoretical conclusion, predicted for very high concentrations of Wurster's red, could be confirmed at lower concentrations of a meriquinone having a higher association constant, as we suggested above that Wurster's blue has. If so, it is

any marked degree to organic solvents, it would not be difficult to imagine that the crystals isolated by Willstätter and Piccard are solid solutions separating from what is virtually a concentrated solution of meriquinone in excess of reductant for the one case and of meriquinone in excess of oxidant in the other case. The compositions of the crystals would then make it appear that tetramethyl p-phenylene diamine can form more than one meriquinone as Willstätter and Piccard thought.

Were this possibility to be confirmed, it would make possible the extension of our formulations in which there is the fundamental assumption that a meriquinone is composed of equal parts of oxidant and reductant. If it is not, or if there remains good reason to believe that a meriquinone can be composed in other proportions, our formulations will remain descriptive of only the simplest type of these peculiar systems, and our data will sketch but the outline of the systems with which we have worked.

In summarizing this section of the paper we believe we can claim that upon the foundations laid in the preceding sections there has been erected a superstructure which will stand. But it is somewhat like the leaning tower of Pisa in that it will bear no more till the foundations are accurately aligned. The discovery of the conditions under which the fundamental constants can be accurately evaluated is the point at which a more comprehensive study than ours must begin.

#### V. General Discussion

Partington (1925), referring to the rather general metastability of organic compounds, remarks "\* \* \* most of the work of the organic chemist is, energetically speaking, skating over thin ice."

The cases at hand are exceptionally beautiful illustrations of this. Although the data leave much to be desired when regarded from the point of view of the physical chemist who seeks apt material with which to obtain accurate equilibrium constants, there is a concordance in the evidence sufficient to indicate that temporary equilibrium states have been roughly defined. It may not be out of place to suggest that the difficulties and inaccuracies met are in large degree due to the element time, which the exigencies of ordinary manipulations impose. A more comprehensive sense of time might make us realize that the systems under discussion differ only in degree from those which give, for somewhat longer periods of time, stable potentials, even though we realize that these last systems are, in an absolute sense, metastable.

Lewis & Randall (1923) remark "\* \* \* as it rarely happens that we are fortunate enough to find a system which is in equilibrium with respect to every possible change, we are content to find the



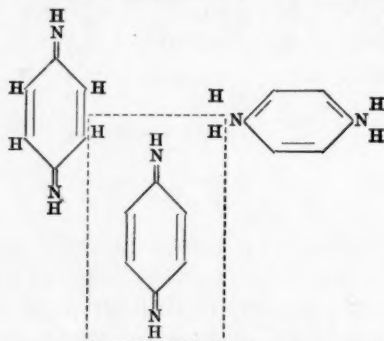
conditions of equilibrium with respect to certain changes, without inquiring whether there may be other processes which are slowly proceeding."

In the cases at hand the "other processes" are by no means slow; but this fact hardly destroys the pertinence of Lewis's remark if it be granted that the experimental method has ridden the "ice" while it held.

What the "other processes" are it is difficult to specify with assurance; but the conduct of the electrode as the "ice" gives way should ultimately be correlated with the organic reactions to the refutation or confirmation of conclusions reached by either method of approach.

We shall, therefore, discuss a partial explanation with which facts so far known agree.

In a variety of instances, too numerous to detail, it has been shown that quinone structures are prone to react with aromatic amines to form anilids. In the cases at hand the reductant is an amine and the oxidant has a quinone structure. Accordingly, the type system could undergo an autoxidation-reduction to form, as a first stage, mono- or di-anilids as illustrated in the following way:



A result of this reaction, in the absence of air, would be the disappearance of the oxidant and the maintenance of the reductant.

Accordingly, the electrode potential should drift toward more negative potentials as the reaction proceeds. This is experimentally true. It is also true that a few measurements made with low percentage oxidation gave more stable potentials, as would be the case were the rate of anilid formation dependent indirectly upon the square of the oxidant concentration.

Furthermore, the system, if protected from air and if examined before decompositions of other types have proceeded too far, should contain an abundance of the reductant. We subjected a solution of Wurster's red to this experiment. When under nitrogen the color characteristic of this meriquinone had disappeared, and there was left only the purple suspension of the reaction products, samples



were withdrawn and oxidized by chlorine-water. There was formed a deep-colored solution as if of Wurster's red. It is unfortunate that we know of no way for *accurate* estimation of the p-amino dimethyl aniline in such circumstances; but titrations suggested the presence of the reductant in concentrations comparable in their order of magnitude with that in the original solution. A similar experiment with the tolidine system, which may be performed with exposure to air because of the slowness of oxidation by air, gave a similar qualitative result.

We doubt that the reactions taking place are as simple as the reaction suggested or that the product suggested would remain without rearrangement; but in addition to such scanty evidence as we have cited, it may be noted that the accidental or purposeful direction of the oxidation of the simple diamines has led to stable dyes in which are found linkages of the type suggested.

Were it not for the complexity of the temporary equilibria, decrements of electrode potential, such as are shown in Table 1, would furnish excellent data for kinetic studies of the processes. Translation of these decrements into decrements of percentage oxidation is comparatively easy in the case of the most acid solution. For the more nearly neutral conditions the complete equation must be used, and then the absolute as well as the relative concentrations of total reductant and total oxidant become important. This not only renders the computations extremely complicated, but will leave them of dubious value until the nature of the decomposition in its effect upon the absolute values of  $[S_r]$  and  $[S_o]$  can be determined with certainty.

The detection and characterization of temporary equilibrium states under the circumstances may be of some significance as one approach to the study of irreversible systems. Had the color ascribed to meriquinones not attracted attention, had it not led to the isolation and description of the immediate oxidation product of the diamine, we would probably be regarding the oxidation of a diamine as an irreversible process leading to a complicated set of oxidation products. An intermediate reversible stage has been definitely established through the investigations of the organic chemist and has been quantitatively defined by the present investigation.

Returning now to the equilibrium studies, we wish to state that it will be well to keep distinct the evidence for temporary equilibrium states and the evidence that these states can be formulated by the equations presented. While it is true that in spite of inevitable inaccuracies there is a reasonable conformity between experimental data and relations implied in the equations, there are noteworthy exceptions. Some of these can be "explained away," but all should be subjected to further study. There are also incomplete aspects

of the data. In particular it should be emphasized that certain relations implied in the equations could be readily tested by a comparison of measurements above and below the pH zone of maximum meriquinone. But, since instability increases rapidly with pH, satisfactory tests could not be made.

Because of incomplete data, because of certain unexplained facts, and particularly because the instability of potentials has left an element of uncertainty in the interpretations given, the formulations had best be regarded as directive hypotheses. Without them we would not have sought some of the relations found. With them we can express in semiquantitative terms the main features of each system and can leave the subject in such a form that subsequent investigators can design where we had to guess conditions for testing special features.

Regarding the formulations as approximate descriptions of general features, it is possible without a lengthy recapitulation of the actual experimental facts, which we shall have in mind during the following discussion, to draw some important conclusions.

For instance, consider a diamine as a reagent for the detection of oxidants.

It is now evident how the pH of the solution plays a part in determining color. In addition it might be mentioned that as regards rate of color-formation by slowly acting oxidants such as molecular oxygen, there is probably a resultant between the accelerating influences of increased pH upon actual oxidation and upon rate of color-fading. Perhaps this has been studied in connection with the controversy over the Storch reaction which Lane-Claypon (1916) mentions; but we recall no systematic investigation of the fact that hydrion concentration has an effect on color production, which Battelli and Stern (1912) mentioned. Some crude experiments which we made yielded a maximum color in the air oxidation of p-phenylene diamine at pH 6.4. This is so near to the normal reaction of milk that it suggests a bearing upon the Storch test which Orla Jensen (1906) states was used in designing the Danish law of pasteurization, passed with the purpose of checking tuberculosis.

If, for the sake of simplicity, we regard the hydrion concentration of the solution to be constant, the oxidation intensity, in terms of potential,  $E_h$ , required to induce the concentration  $[M]$  can be defined by

$$E_h = E'_0 - \frac{RT}{2F} \ln \frac{[S_r] - [M]}{[S_o] - [M]}$$

While  $[S_r]$  remains large in comparison with  $[S_o]$ , and when the pH value chosen is such that the tendency to the formation of meriquinone will result in the value of  $[M]$  approaching  $[S_o]$ ,  $E_h$  will be

very much more negative than would be expected of an ordinary, slightly oxidized system. According to the more complete equations given in Section III,  $[M]$  is not only a function of pH, of the meriquone association constant, and of the ratio of total oxidant to total reductant, but also of the absolute concentrations of oxidant and reductant.

In short, there are several conditions to be met if an oxidant is to induce a definite color; and, conversely, by variation of these conditions the potential necessary can be made to vary. By reason of the greater solubility of the components of the p-phenylene diamine series and the larger meriquone association constant, the latitude of variability is greater in these systems than it is in the case of members of the benzidine series.

It is, therefore, evident that Kolthoff's (1924) treatment of the subject was premature.

Now, of course, it is recognized that there is no *unique* specificity (other than that associated with the formation of specific salts) which is exhibited by these reagents; but the rather high characteristic potentials of these systems imply certain limitations upon the number of oxidizing systems which possess the potentials necessary to induce a definite degree of color. However, there has just been mentioned the possibility of varying the conditions with consequent variation in the potentials required. Consequently there arise two questions of importance to analytical chemistry: First, has the enormous amount of labor expended upon the empirical standardization of certain uses of these reagents established the conditions within which reproducible results can be obtained? Second, is it worth while to apply to these precarious reagents the logical standardization of conditions which our equations implicitly outline?

An interesting case in which empiricism has led to the avoidance of difficulties which can now be explained is that of the o-tolidine test for free chlorine, used in the control of water disinfection.

Originally the meriquone color was sought. Variation in the ratio of o-tolidine base to hydrochloric acid in the "hydrochloride" and more particularly variation in the "alkalinity" of natural waters produced a considerable variation in the pH of the mixture. Different degrees of oxidation which were then induced by the chlorine were superimposed upon the effects of variable pH and inevitably produced a troublesome variation both in quality and amounts of color. Ellms & Hauser (1913) found that the use of strongly acid solutions resulted in a more permanent yellow of more uniform gradation proportional to the chlorine added. The explanation is now perfectly evident. A return to the blue color test would be useful in the examination of colored waters and could now be logically designed, but it is improbable that the specifications would be simple enough for field use.

In tests where a meriquinone color is still employed, the failure to adhere to rigid specifications, or the failure in point of adequacy of specifications, should result in a variability of color. This would not be evident in rough qualitative tests but would become evident in quantitative studies. But, if a qualitative test be regarded as quantitative within limits, the danger in the qualitative uses of these reagents becomes apparent.

In cases where color-production is slow, as it is in many biological applications of these reagents, another difficulty must be considered. The situation already discussed still applies. In addition, the lapse of time permits the withdrawal of total oxidant by condensation processes, suppresses the value of the denominator in the ratio  $\frac{[S_0] - [M]}{[S_0] - [M]}$ , and may permit a very low value of  $E_h$ . In other words, a destructive oxidation, destructive in the sense of the gradual disappearance of the reagent and its immediate products of oxidation, can be induced by systems of very low oxidation intensity. A factor determining this now becomes the rate of the condensation, for upon the relation between this rate and the rate of the slow oxidation depends the ratio stated above.

Now some of the condensation products are colored; and although they tend to precipitate in ordinary aqueous solutions they remain in suspension, or as Bach (1915) noted in the case of the colored oxidation product or products of p-phenylene diamine they may remain absorbed in the suspended, formed elements of biological preparations. It, therefore, becomes quite essential to determine whether the color found is that of a true meriquinone or that of some condensation product. If of the former, interpretation is simplified. If of the latter, interpretation is difficult. For instance it can be imagined that the biological material can catalyze the condensation process as it is known to catalyze a similar condensation in the formation of indamines. If so, the production of the more complex colors would be determined in part by a process having little to do directly with acceleration of oxygenations.

We would not agree that this hypothesis is fair in its implications regarding the so-called peroxidase and other tests in which diamines are employed as test reagents, but the value of the hypothesis lies in its ability to illustrate two matters of more general importance.

Firstly, the hypothetical case presented is one of those extremely complicated results which may follow the employment of a reaction composed of reversible and irreversible phases. Secondly, it is just such complications that injure the value of many color tests. A color reaction to be safe must respond to one definite set of conditions and to one only. In the future this elementary principle will guide the design of reagents, and these reagents will be intelligently con-

structed from the wealth of resources in organic synthesis, and will not be mere by-products of organic chemistry.

Our objective is now attained. We have found the potentiometric method applicable. It has furnished a definite basis of fact for a conclusion regarding the reliability of these reagents, and we must conclude that both the instability and the complexity of the systems will render them of little practical importance for precise studies of biological oxidation-reduction.

On the other hand, the results are, we believe, of considerable value not only to the problem of meriquinones but also as concrete illustrations of several phenomena which will undoubtedly be encountered as the method is extended. We have left a formulation which can readily be submitted to more extended or more detailed study. If necessary it can be elaborated so that certain biological applications of the reagents can be logically controlled and more precise deductions drawn; but for the reason stated above the subject will henceforth be almost exclusively one of organic chemistry.

## VI. Summary

On the assumption that a meriquinone is composed of equal parts of oxidant and reductant, there has been formulated the following relation between the potential difference,  $E_h$ , at an electrode, and the meriquinone concentration  $[M]$ , the concentration of total reductant  $[S_r]$ , the concentration of total oxidant  $[S_o]$ , the hydron concentration  $[H^+]$ , and the several dissociation constants of oxidant and reductant  $K_{r1}$ ,  $K_{r2}$ ,  $K_{o1}$ ,  $K_{o2}$ , which are defined below.

$$E_h = E_o - \frac{RT}{2F} \ln \frac{[S_r] - [M]}{[S_o] - [M]} + \frac{RT}{2F} \ln \frac{K_{r1}K_{r2} + K_{r2}[H^+] + [H^+]^2}{K_{o1}K_{o2} + K_{o2}[H^+] + [H^+]^2} - \frac{RT}{F} \ln \frac{1}{[H^+]}$$

(I)
(II)
(III)
(IV)

All potentiometric measurements were made at 30° C.

In one series of experiments  $[H^+]$  was kept constant at a value sufficiently high in relation to the constants of term III to practically eliminate this term and also sufficiently high to make  $[M]$  of term II negligible in relation to  $[S_r]$  and  $[S_o]$ . Under these circumstances o-tolidine, benzidine, and p-amino dimethylaniline were titrated with dilute chlorine-water and were found to furnish the ordinary type of "titration curve." In short the equation was reduced to

$$E_h = E_o - \frac{RT}{2F} \ln \frac{[S_r]}{[S_o]} - \frac{RT}{F} \ln \frac{1}{[H^+]}$$

Then, since  $[H^+]$  was known from the value of the buffer used and the ratio  $\frac{[S_r]}{[S_o]}$  was determined by the stages of the titration,  $E_o$ , the



first term of the equation was evaluated. There were found the following values:

System of—	$E_0$ ("normal potential")
o-Tolidine.....	+0.873
Benzidine.....	+ .921
p-Amino dimethylaniline.....	+ .751

Studies at lower acidities than those used in the above experiments were rendered very difficult by the rapid drifts of potentials. Indeed, these were so rapid that in partially oxidized solutions of tetramethyl p-phenylene diamine, p-phenylene diamine, a benzidine sulfonate, and a chloro benzidine no reliable measurements were obtained. However, by rapid operations with o-tolidine, benzidine, and p-amino dimethyl aniline there were found "initial" potentials which could be reasonably interpreted. Since at 50 per cent oxidation term II reduces to zero, a second series of measurements was made under this condition and the initial potentials then observed seemed very definitely to reveal the effects of dissociations, the constants of which appear in term III. Certain inflections of the curve relating  $E_h$  to pH, the so-called  $E'_0$  : pH curve, at 50 per cent oxidation corresponded with what would be expected of two dissociations of the reductant the constants of which were determined by hydrogen electrode titrations.

These hydrogen electrode measurements furnished the following values:

Substance	Dissociation constants	
	First basic	Second basic
o-Tolidine.....	$6.2 \times 10^{-10}$	$2.9 \times 10^{-11}$
Benzidine.....	$9.3 \times 10^{-10}$	$5.6 \times 10^{-11}$
p-Amino dimethylaniline.....	$3.9 \times 10^{-9}$	$8.0 \times 10^{-12}$

For convenience these constants, as well as those of the oxidant, were transformed to meet the following definitions of the constants appearing in term III of the main equation.

$$\frac{[\text{Red}][\text{H}^+]}{[\text{HRed}]} = K_{r1}; \quad \frac{[\text{HRed}][\text{H}^+]}{[\text{H}_2\text{Red}]} = K_{r2}; \quad \frac{[\text{OxOH}][\text{H}^+]}{[\text{Ox}]} = K_{o2};$$

$$\frac{[\text{Ox}(\text{OH})_2][\text{H}^+]}{[\text{OxOH}]} = K_{o1}.$$

When  $[\text{S}_r] = [\text{S}_o]$  the main equation reduces to

$$E_h = E_0 - \frac{RT}{F} \ln \frac{1}{[\text{H}^+]}, \quad \text{at high values of } [\text{H}^+],$$



while at low values of  $[H^+]$  it reduces to

$$E_h = E_o - \frac{RT}{F} \ln \frac{1}{[H^+]} + \frac{RT}{2F} \ln \frac{K_{r1} K_{r2}}{K_{o1} K_{o2}}$$

Since  $K_{r1}$  and  $K_{r2}$  were determined by hydrogen electrode measurements, the product  $K_{o1} K_{o2}$  was found from the above equations, in the cases of the o-tolidine and p-amino dimethyl-aniline systems. By assumptions outlined in the text the individual values of  $K_{o1}$  and  $K_{o2}$  which were taken to solve the equation numerically were as follows:

Diimine of—	$K_{o1}$	$K_{o2}$
o-Tolidine.....	$6.9 \times 10^{-7}$	$1.4 \times 10^{-4}$
p-Amino dimethyl aniline.....	$4.0 \times 10^{-3}$	$2.0 \times 10^{-4}$

The curves constructed by means of the main equation which now could be solved numerically were found to be in reasonable agreement with the experimental values.

For the solution of the equation when  $[S_r]$  does not equal  $[S_o]$  it is necessary to know the values of  $[M]$  under any given set of circumstances.

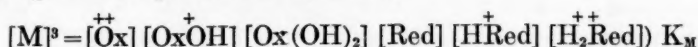
There was developed the following equation:

$$2[M] = [S_r] + [S_o] + K'w - \sqrt{([S_r] + [S_o] + K'w)^2 - 4[S_r][S_o]}$$

$$\text{where } w = \frac{(K_{r1}K_{r2} + K_{r2}[H^+] + [H^+]^2)(K_{o1}K_{o2} + K_{o2}[H^+] + [H^+]^2)}{[H^+]^2}$$

$$\text{and where } K' = \frac{1}{\sqrt{K_{r1}K_{o1}(K_{r2})^2(K_{o2})^2K_M}}$$

$K_M$ , in turn, being defined as the association constant determining the extent to which the meriquinone forms from all constituents according to the equilibrium equation,



For purposes of comparison with ordinary association constants the cube roots of  $K_M$  were compared. They were found to be  $1.5 \times 10^6$  for the meriquinone of o-tolidine and  $1.1 \times 10^9$  for the meriquinone of p-amino dimethyl aniline (Wurster's red).

These values were obtained by potentiometric measurements of the displacements of potentials, at fixed percentage oxidation at known values of  $[H^+]$ , from the potentials calculated for a case in which no meriquinone forms to withdraw the various forms of oxidant and reductant.

With  $[M]$  made determinable it was shown that it is possible to obtain confirmatory data by assuming that the color of solutions is the resultant of the color due to the meriquinone and to the residual holoquinone. To do this accurately the highest precision in the evaluation of constants entering the equations was shown to be

necessary and it was emphasized that this requirement had not been met because of the experimental difficulties attending the study of these highly unstable systems. Nevertheless rough confirmations were made by means of spectrophotometric and colorimetric measurements.

Spectrophotometric absorption curves for the meriquinones of o-tolidine, p-amino dimethyl aniline and tetramethyl p-phenylene diamine were determined. The curve of the meriquinone of o-tolidine shows a maximum absorption at  $\mu\mu$  630. Wurster's red shows two absorption maxima, one at  $\mu\mu$  520 and the other at  $\mu\mu$  550. Likewise Wurster's blue shows two maxima, one at  $\mu\mu$  565 and the other at  $\mu\mu$  615. The colors of the solutions in the presence of various proportions of the respective holoquinone were discussed.

A peculiarity which, the equations imply, should occur at high concentrations of a system, the meriquinone of which has a very high association constant, was theoretically discussed. This peculiarity is the virtual separation of the system into two, one of which is meriquinone in excess of reductant and the other meriquinone in excess of oxidant.

The bearing of the data and conclusions upon the use of color reactions involving the meriquinone colors was briefly discussed. The complexity of the equilibria, not to mention the instability of the systems, will make difficult the use of the data in a logical development of standard conditions suitable for one or another of the various color reactions. The cause of the instability of the systems was touched upon. Tentatively assuming that it is due in part to an autoxidation in which anilid-like compounds are formed, it was shown that the occurrence of any such process would make extremely dangerous the drawing of ordinary conclusions from color reactions with benzidine, p-phenylene diamine and their homologues.

### VII. Tables

TABLE 1.—Drifts of potential.  $9 \times 10^{-5}$  M ortho-tolidine initially 50 per cent oxidized with chlorine water

Solution No. 3; pH 1.99			Solution No. 6; pH 3.29			Solution No. 8; pH 4.43		
Time	E <sub>h</sub>	Decrement	Time	E <sub>h</sub>	Decrement	Time	E <sub>h</sub>	Decrement
Minutes	Volts	Millivolts	Minutes	Volts	Millivolts	Minutes	Volts	Millivolts
0	0.7533	-----	0	0.6821*	-----	0	0.6377	-----
0.5	.7538	-----	1.5	.6815	0.6	0.5	.6344	3.3
1.0	.7538	-----	2.0	.6810	1.1	1.0	.6315	6.2
6	.7534	0.4	2.5	.6807	1.4	2.0	.6240	13.7
11	.7528	1.0	4.0	.6798	2.3	3.0	.6178	19.9
17	.7520	1.8	6.0	.6775	4.6	7.5	.6099	36.8
20	.7514	2.4	9.0	.6748	7.3	11.0	.5893	48.4
30	.7497	4.1	12.5	.6715	10.6	20	.5691	68.6
59	.7427	11.1	14	.6686	13.5	83	.4848	152.9
117	.7201	33.7	19	.6634	18.7			
			44	.6365	46.6			

\*Extrapolated.

TABLE 2.—Titration of *o*-tolidine (50 c.c. 0.0001 M) with chlorine water (0.001 N), pH 1.05, Temp. 30° C.

[Total time of titration, 17 minutes. Observer A]

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E'_o$
<i>C. c.</i>	<i>Per cent</i>			
0	0		0.697	
1	10	+0.0287	.7807	0.8094
2	20	.0181	.7910	.8091
3	30	.0111	.7981	.8092
4	40	+ .0053	.8039	.8092
5	50	.0000	.8090	.8090
6	60	-.0053	.8143	.8090
7	70	-.0111	.8202	.8091
8	80	-.0181	.8276	.8095
9	90	-.0287	.8396	(.8109)
10	100			

Average= 0.8092

 $\pi_h = -.0631$  $E_o = 0.8723$ TABLE 3.—Titration of *o*-tolidine (50 c.c. 0.0001 M) with chlorine-water (approx. 0.0008 N), pH 1.05, Temp. 30° C.

[Total time of titration, 13 minutes. Observer A]

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E'_o$
<i>C. c.</i>	<i>Per cent</i>			
2	15.75	+0.0219	0.7881	0.8100
3	23.62	+ .0153	.7946	.8099
4	31.50	+ .0101	.7996	.8097
5	39.37	+ .0056	.8039	.8095
6	47.24	+ .0014	.8081	.8095
7	55.11	-.0027	.8120	.8093
8	62.99	-.0069	.8161	.8092
9	70.86	-.0116	.8208	.8092
10	78.73	-.0171	.8263	.8092
11	86.62	-.0244	.8339	.8095
12.7	100.00			

Average= 0.8095

 $\pi_h = -.0631$  $E_o = 0.8726$ TABLE 4.—Titration of *o*-tolidine (50 c.c. 0.0001 M) with chlorine-water (approx. 0.00075 N), pH 1.05, Temp. 30° C.

[Total time of titration, 19 minutes. Observer A]

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E'_o$
<i>C. c.</i>	<i>Per cent</i>			
1	7.35	+0.0331	+0.7751	0.8082
2	14.70	.0229	.7857	.8086
3	22.06	.0165	.7921	.8086
4	29.41	.0114	.7971	.8085
5	36.76	.0071	.8013	.8084
6	44.12	+ .0031	.8052	.8083
7	51.47	-.0008	.8087	.8079
8	58.82	-.0047	.8124	.8077
9	66.18	-.0088	.8164	.8076
10	73.53	-.0133	.8208	.8075
11	80.88	-.0188	.8265	.8077
12	88.24	-.0263	.8344	.8081
13.6	100.00			

Average= 0.8081

 $\pi_h = -.0631$  $E_o = 0.8712$

TABLE 5.—*Titration of o-tolidine (50 c. c. 0.0001 M) with chlorine-water (approx. 0.0008 N), pH 1.37, Temp. 30° C.*

[Total time of titration 17 minutes. Observer A]

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E_o$
<i>C. c.</i>	<i>Per cent</i>			
1	7.87	+0.0321	0.7598	0.7919
2	15.75	+ .0219	.7698	.7917
3	23.62	+ .0153	.7761	.7914
4	31.50	+ .0101	.7812	.7913
5	39.37	+ .0056	.7854	.7910
6	47.24	+ .0014	.7893	.7907
7	55.11	— .0027	.7932	.7905
8	62.99	— .0069	.7972	.7903
9	70.86	— .0116	.8017	.7901
10	78.73	— .0171	.8070	.7899
11	86.62	— .0244	.8141	.7897
12.7	100.00	-----	-----	-----

Average = 0.7908

 $\pi_h = -.0823$  $E_o = 0.8731$ TABLE 6.—*Titration of o-tolidine (50 c. c. 0.0001 M) with chlorine-water (approx. 0.0008 N), pH 1.985, Temp. 30° C.*

[Total time of titration 15 minutes. Observer A]

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E_o$
<i>C. c.</i>	<i>Per cent</i>			
1	7.87	0.0321	0.7225	0.7546
2	15.75	.0219	.7327	.7546
4	31.50	.0101	.7440	.7541
5	39.37	.0056	.7482	.7538
6	47.24	+ .0014	.7522	.7536
7	55.11	— .0027	.7560	.7533
8	62.99	— .0069	.7600	.7531
10	78.73	— .0171	.7700	.7529
12	94.50	— .0371	.7916	.7545
12.7	100.00	-----	-----	-----

Average = 0.7538

 $\pi_h = -.1193$  $E_o = 0.8731$ TABLE 7.—*Titration of o-tolidine (50 c. c. 0.0001 M) with chlorine-water (approx. 0.0005 N), pH 2.866, Temp. 30° C.*

[Total time of titration, 18 minutes. Observer B]

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E_o$
<i>C. c.</i>	<i>Per cent</i>			
2	8.2	0.0315	0.6650	0.6965
4	16.3	.0214	.6774	.6988
6	24.5	.0147	.6852	.6999
8	32.7	.0094	.6910	.7004
10	40.8	.0048	.6961	.7009
12	49.0	+ .0005	.7010	.7015
14	57.1	— .0037	.7058	.7021
16	65.3	— .0083	.7109	.7026
18	73.5	— .0133	.7164	.7031
20	81.6	— .0195	.7234	.7039
22	89.8	— .0284	.7334	.7050
24	98.0	— .0508	.7511	.7003
24.5	100.0	-----	-----	-----

Average = 0.7013

 $\pi_h = -.1722$  $E_o = 0.8735$

TABLE 8.—*o*-Tolidine. Relation of  $E'_o$  to pH (Series I). 50 c. c. 0.0001 *M* tolidine in buffer + 2 c. c. Cl-water = 41 per cent oxidation. Hence add 0.0047 to  $E_h$  to obtain  $E'_o$ .

Buffer No.	pH	$E_h$	$E'_o$	$E_o$
1.....	1.08	0.8039	0.809	0.873
2.....	1.37	.7857	.790	.872
3.....	1.99	.7481	.753	.872
4.....	2.43	.7234	.728	(.874)*
5.....	2.87	.6961	.701	(.873)*

\*Uncorrected for dissociations

Average = 0.872

TABLE 9.—*o*-Tolidine. Relation of  $E'_o$  to pH (Series II). 50 c. c. 0.0001 *M* tolidine in buffer + 2 c. c. Cl-water = 42 per cent oxidation

Buffer No.	pH	$E_h$	$E'_o$	$E_o$
N/5 HCl.....	*0.70	0.8267	0.831	0.873
1.....	1.08	.8038	.808	.873
2.....	1.37	.7847	.789	.871
3.....	1.99	.7486	.753	.872
4.....	2.43	.7239	.728	*(.874)
5.....	2.87	.6995	.704	*(.876)

\*Assuming complete dissociation

Average = 0.872

\*\*Uncorrected for dissociation.

TABLE 10.—*o*-Tolidine. Relation of  $E'_o$  to pH (Series III and IV). 50 c. c. 0.0001 *M* tolidine in buffer + indicated amount of Cl-water

Series	Buffer No.	pH	End-point	$E_h$			$E'_o$	$E_o$
				With 6 c. c.	With 6.5 c. c.	With 6.75 c. c.		
			C. c.					
III	1.....	1.05	13.6	0.8052	-----	-----	0.808	0.871
IV	1.....	1.05	12.7	.8061	-----	-----	.810	.874
IV	2.....	1.37	12.7	.7893	-----	-----	.791	.873
IV	3.....	1.99	12.7	.7522	-----	-----	.754	.873
IV	4.....	2.43	12.7	.7265	-----	-----	.728	.874
IV	5.....	2.87	12.7	.7010	-----	-----	.702	-----
IV	6.....	3.29	12.7	.6798	-----	-----	.681	-----
IV	7.....	3.80	12.7	-----	0.664	-----	.663	-----
IV	8.....	4.43	12.7	-----	.643	-----	.642	-----
IV	9.....	4.88	12.7	-----	.635	-----	.634	-----
IV	10.....	5.34	12.7	-----	.625	-----	.624	-----
IV	11.....	5.92	12.7	-----	.613	-----	.612	-----
IV	13.....	6.27	12.7	-----	.588	-----	.587	-----
III	14.....	6.70	13.6	-----	-----	0.567	.567	-----
III	15.....	6.95	13.6	-----	-----	.553	.553	-----
III	16.....	7.55	13.6	-----	-----	.518	.518	-----
III	20.....	8.20	13.6	-----	-----	.499	.499	-----

Average = 0.873

TABLE 11.—*Titration of 50 c. c. 0.00103 M o-tolidine dihydrochloride with 0.005 N NaOH. Hydrogen electrode 30° C*

$$C = \frac{0.00103 \times 50}{V}$$

$$B_t = \frac{0.005 \times \text{c. c. NaOH}}{V}$$

$$B'_1 = B_t - B'_2$$

$$B''_1 = B_t - B''_2$$

$$B'_2 = \frac{C \times 3 \times 10^{-4}}{[H^+] + (3 \times 10^{-4})}$$

$$B''_1 = \frac{C \times 6.5 \times 10^{-4}}{[H^+] + (6.5 \times 10^{-4})}$$

$$pK'_1 = \log [H^+] + \log (B'_1 + [H^+]) - \log (C - B'_1 - [H^+])$$

$$pK''_1 = \log [H^+] + \log (B''_1 + [H^+]) - \log (C - B''_1 - [H^+])$$

NaOH	Volume (V)	C×10 <sup>3</sup>	pH	[H <sup>+</sup> ]×10 <sup>4</sup>	B <sub>t</sub> ×10 <sup>3</sup>	B' <sub>1</sub> ×10 <sup>3</sup>	B' <sub>2</sub> ×10 <sup>3</sup>	B' <sub>1</sub> + [H <sup>+</sup> ]×10 <sup>4</sup>
C. c.								
0	50	103	3.211	62	0	5	-5	57
1	51	101	3.279	53	10	5	5	58
2	52	99	3.343	45	19	6	13	58
3	53	97	3.411	39	28	7	21	60
4	54	95	3.479	33	37	8	29	62
5	55	94	3.554	28	45	9	36	64
6	56	92	3.634	23	54	11	43	66
7	57	90	3.717	19	61	12	49	68
8	58	89	3.804	16	69	14	55	71
9	59	87	3.899	13	76	16	60	73
10	60	86	3.965	10	83	19	64	74
11	61	84	4.100	7.9	90			
12	62	83	4.208	6.2	97			
13	63	82	4.316	4.8	103			
14	64	80	4.436	3.7	109			
15	65	79	4.564	2.7	115			
16	66	78	4.699	2.0	121			
17	67	77	4.857	1.4	127			
18	68	76	5.052	.89	132			
19	69	75	5.31	.49	138			
20	70	74	5.81	.15	143			
20.6								

NaOH	C-B' <sub>1</sub> -[H <sup>+</sup> ]×10 <sup>3</sup>	pK' <sub>1</sub>	B'' <sub>1</sub> ×10 <sup>3</sup>	B'' <sub>2</sub> ×10 <sup>3</sup>	B'' <sub>1</sub> + [H <sup>+</sup> ]×10 <sup>4</sup>	C-B'' <sub>1</sub> -[H <sup>+</sup> ]×10 <sup>3</sup>	pK'' <sub>1</sub>
C. c.							
0	46	3.12					
1	43	3.15					
2	41	3.19					
3	37	3.20					
4	33	3.21					
5	30	3.13					
6	26	3.23					
7	22	3.23					
8	18	3.21					
9	14	3.18					
10	12	3.21					
11			75	8	18	68	(4.57)
12			75	15	23	61	4.52
13			76	21	27	56	4.53
14			76	27	32	50	4.51
15			75	34	38	42	4.48
16			76	39	42	37	4.51
17			76	45	47	31	4.52
18			76	51	52	25	4.54
19			75	57	58	18	4.54
20			75	63	63	12	(4.59)
20.6			74	69	69	5	(4.67)

Average=3.19

Average=4.52



TABLE 12.—*Titration of 50 c. c. 0.0001 molar benzidine in buffer of pH 1.08 with chlorine-water*

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E'$
<i>C. c.</i>	<i>Per cent</i>			
2	17.4	+0.0203	+0.835	0.855
4	34.8	.0082	.847	.855
5	43.5	.0034	.852	.855
6	52.2	— .0011	.856	.855
7	60.9	— .0058	.860	.854
8	69.6	— .0108	.864	.853
10	87.0	— .0248	.875	(.850)
11.5	100.0	-----		

$$\text{Average} = 0.855$$

$$\pi_h = -.065$$

$$E_o = +0.920$$

TABLE 13.—*Titration of 50 c. c. 0.0001 molar benzidine in buffer of pH 1.37 with chlorine-water*

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E'$
<i>C. c.</i>	<i>Per cent</i>			
1	8.7	+0.0307	0.809	0.840
2	17.4	+ .0203	.820	.840
3	26.1	+ .0136	.826	.840
4	34.8	+ .0082	.832	.840
5	43.5	+ .0034	.837	.840
6	52.2	— .0011	.841	.840
7	60.9	— .0058	.846	.840
8	69.6	— .0108	.850	.839
9	78.3	— .0168	.856	.839
10	87.0	— .0248	.863	(.838)
11.5	100.0	-----		

$$\text{Average} = +0.840$$

$$\pi_h = -.082$$

$$E_o = +0.922$$

TABLE 14.—*Titration of 50 c. c. 0.0001 molar benzidine in buffer of pH 1.99 with chlorine-water*

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E'$
<i>C. c.</i>	<i>Per cent</i>			
2	17.4	+0.0203	0.782	0.802
4	34.8	.0082	.794	.802
5	43.5	.0034	.799	.802
6	52.2	— .0011	.803	.802
7	60.9	— .0058	.808	.802
8	69.6	— .0108	.813	.802
10	87.0	— .0248	.828	.803
11.5	100.0	-----		

$$\text{Average} = +0.802$$

$$\pi_h = -.120$$

$$E_o = 0.922$$

TABLE 15.—*Titration of 50 c. c. 0.0001 molar benzidine in buffer of pH 2.43 with chlorine-water. (30° C.)*

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E'_o$
<i>C. c.</i>	<i>Per cent</i>			
2	17.4	+0.0203	+0.755	0.775
4	34.8	.0082	.768	.776
5	43.5	.0034	.772	.775
6	52.2	— .0011	.777	.776
7	60.9	— .0058	.781	.775
8	69.6	— .0108	.786	.775
10	87.0	— .0248	.799	(.774)
11.5	100.0	-----	-----	-----

Average = 0.775

 $\pi_h = -.146$  $E_o = 0.921$ TABLE 16.—*Titration of 50 c. c. 0.0001 molar benzidine in buffer of pH 3.29 with chlorine-water (30° C.)*

Cl-water	Oxidation	$0.03006 \log \frac{[S_r]}{[S_o]}$	$E_h$	$E'_o$
<i>C. c.</i>	<i>Per cent</i>			
4	34.8	+0.0082	0.719	0.727
6	52.2	— .0011	.727	.726
7	60.9	— .0058	.731	.725
8	69.6	— .0108	.735	.724
11.5	100.0	-----	-----	-----

Average = 0.726

 $\pi_h = -.198$  $E_o = 0.924$ 

\* Uncorrected for effect of dissociation.

TABLE 17.—*Benzidine. Relation of  $E'_o$  to pH. 50 c. c. 0.0001 M benzidine in buffer + Cl-water to induce 50 per cent oxidation*

pH	First series		Second series	
	$E'_o$	$E_o$	$E'_o$	$E_o$
1.08	0.855	0.920	0.855	0.920
1.37	.840	.922	.839	.921
1.99	.802	.922	.802	.922
2.43	.775	.921	.776	.922
2.87	-----	-----	.750	.922
3.29	.730	-----	.726	-----
3.80	.714	-----	.702	-----
4.43	.677	-----	.674	-----
4.88	.650	-----	.672	-----
5.34	.637	-----	.632	-----
5.92	.611	-----	.612	-----

Average = 0.921

TABLE 18.—Titration of 50 c. c. 0.00102 molar benzidine dihydrochloride with 0.005 N NaOH. Hydrogen electrode 30° C.

$C = \frac{0.00102 \times 50}{V}$		$B'_1 = \frac{C(2 \times 10^{-4})}{[H^+] + (2 \times 10^{-4})}$	
$B_r = \frac{0.005 \times \text{cc. NaOH}}{V}$		$B''_1 = \frac{C(3.3 \times 10^{-4})}{[H^+] + (3.3 \times 10^{-4})}$	
$B'_1 = B_r - B'_1$		$pK'_1 = \log[H^+] + \log(B'_1 + [H^+]) - \log[C - B'_1 - [H^+]]$	
$B''_1 = B_r - B''_1$		$pK'_2 = \log[H^+] + \log(B''_1 + [H^+]) - \log[C - B''_1 - [H^+]]$	

NaOH	pH	$[H^+] \times 10^6$	Volume (V)	$C \times 10^6$	$B_r \times 10^6$	$B'_1 \times 10^6$
<i>Cubic centimeters</i>						
0.....	3.338	45.9	50	102	0	4.3
1.....	3.399	39.9	51	100	9.8	4.8
2.....	3.464	34.4	52	98.1	19	5.4
3.....	3.534	29.2	53	96.2	28	6.2
4.....	3.611	24.5	54	94.4	37	7.1
5.....	3.691	20.4	55	92.7	45	8.3
6.....	3.775	16.8	56	91.1	54	9.7
7.....	3.865	13.7	57	89.5	61	11.4
8.....	3.961	10.9	58	87.9	69	13.6
9.....	4.064	8.63	59	86.4	76	16.2
10.....	4.168	6.79	60	85.0	83	19.3
						$B''_1 \times 10^6$
10.....	4.168	6.79	60	85.0	83	70.5
11.....	4.280	5.25	61	83.6	90	72.1
12.....	4.396	4.02	62	82.3	97	73.4
13.....	4.511	3.08	63	81.0	103	74.1
14.....	4.634	2.32	64	79.7	109	74.5
15.....	4.764	1.72	65	78.5	115	74.6
16.....	4.911	1.23	66	77.3	121	74.5
17.....	5.072	0.85	67	76.1	127	74.2
18.....	5.271	0.54	68	75.0	132	73.8
19.....	5.553	0.28	69	73.9	138	73.3

NaOH	$B'_1 \times 10^6$	$B'_1 + [H^+] \times 10^6$	$C - B'_1 - [H^+] \times 10^6$	pK <sub>1</sub>
<i>Cubic centimeters</i>				
0.....	-4.3	41.6	60.4	3.50
1.....	+5.0	44.9	55.1	3.49
2.....	13.6	48.0	50.1	3.48
3.....	21.8	51.0	45.2	3.48
4.....	29.9	54.4	40.0	3.48
5.....	36.7	57.1	35.6	3.49
6.....	44.3	61.1	30.0	3.47
7.....	49.6	63.3	26.2	3.48
8.....	55.4	66.3	21.6	3.47
9.....	59.8	68.4	18.0	3.48
10.....	63.7	70.5	14.5	3.48
				3.48 average = $3.31 \times 10^{-4}$
	$B''_1 \times 10^6$	$B''_1 + [H^+] \times 10^6$	$C - B''_1 - [H^+] \times 10^6$	pK <sub>2</sub>
10.....	12.5	19.3	65.7	4.70
11.....	17.9	23.2	60.4	4.70
12.....	23.6	27.6	54.7	4.69
13.....	28.9	32.0	49.0	4.70
14.....	34.5	36.8	42.9	4.70
15.....	41.4	43.1	35.4	4.68
16.....	46.5	47.7	29.6	4.70
17.....	52.8	53.7	22.4	4.69
18.....	58.2	58.7	16.3	4.71
19.....	64.7	65.0	8.9	4.69
				4.70 average = $2.0 \times 10^{-4}$

TABLE 19.—First section of titration of 0.015 molar *p*-amino dimethyl aniline with 0.08 normal HCl (30° C.)

HCl	pH	Neutralization of base; first stage	$\log \frac{\%}{100-\%}$	pK <sub>1</sub>
<i>C. c.</i>		<i>Per cent.</i>		
0	9.04	0		
0.5	7.47	6.67	-1.146	6.32
1.0	7.14	13.33	-0.813	6.33
1.5	6.93	20.00	-0.602	6.33
2.0	6.76	26.67	-0.439	6.32
2.5	6.62	33.33	-0.301	6.32
3.0	6.49	40.00	-0.176	6.31
3.5	6.38	46.67	-0.058	6.32
4.0	6.26	53.33	+0.058	6.32
4.5	6.14	60.00	0.176	6.32
5.0	6.02	66.67	0.301	6.32
5.5	5.89	73.33	0.439	6.33
6.0	5.73	80.00	0.602	6.33
6.5	5.53	86.67	0.813	(6.34)*
6.8	5.38	90.66	0.987	(6.37)*
7.0	5.24			
7.2	5.06			
7.4	4.80			
7.5	4.63	100.00		

\*Interference by 2d dissociation.

Average=6.32.

pK<sub>b1</sub>=13.73-6.32=7.41.TABLE 20.—Second section of titration of 0.015 molar *p*-amino dimethyl aniline with 0.08 normal HCl. Result of first section treated as presence of neutral salt. Complete dissociation of chloride assumed.

$$\text{Hence } pK_{b1} = \log \frac{[H^+](C - [H^+])}{[HCl]K_w}$$

C = molar concentration of base.

 $K_w = 1.88 \times 10^{-14}$  at 30° C.

HCl (total)	HCl 2d stage	Volume	HCl molar conc.	C	pH obs.	[H <sup>+</sup> ]	C-[H <sup>+</sup> ]	pK <sub>b1</sub>
<i>C. c.</i>	<i>C. c.</i>	<i>C. c.</i>						
7.5	0	67.5			4.63	0.00002		
7.7	0.2	67.7	0.00024	0.00886	4.20	.00006	0.00860	11.09
8.0	0.5	68.0	.00059	.00882	3.79	.00016	.00866	11.10
8.5	1.0	68.5	.00117	.00876	3.46	.00035	.00841	11.12
9.0	1.5	69.0	.00174	.00870	3.26	.00055	.00815	11.14
10.0	2.5	70.0	.00287	.00857	3.01	.00098	.00759	11.14
11.0	3.5	71.0	.00394	.00845	2.85	.00141	.00704	11.13
12.0	4.5	72.0	.00500	.00833	2.72	.00191	.00642	11.11
13.0	5.5	73.0	.00603	.00822	2.62	.00240	.00582	11.09
14.0	6.5	74.0	.00703	.00811	2.54	.00288	.00523	11.06
15.0	7.5	75.0	.00800	.00800	2.47	.00339	.00461	11.04

Average=11.10

TABLE 21.—Meriquinone of tolidine. Calculations of percentages of maximum meriquinone and of meriquinone association constant from potential deviations (30° C.)

$$K_{r_1} = 3 \times 10^{-3}; K_{r_2} = 6.5 \times 10^{-4}; K_{o_1} = 6.9 \times 10^{-7}$$

$$K_{o_2} = 1.4 \times 10^{-3}; [S_r] = 1.87 \times 10^{-3}; [S_o] = 4.0 \times 10^{-3}$$

Sol. No.	pH	log w	E'.	E <sub>h</sub>	E' - E <sub>h</sub>	[M] × 10 <sup>3</sup>	%[M]	E' - E <sub>h</sub> - .03006 log $\frac{[S_r]}{[S_o]}$	Z	K'
3	1.993	4.0416	0.7540	0.7005	0.0535	0.85	21.5	0.0031	1.27	(63)
4	2.437	5.1994	.7286	.6753	.0533	1.95	49.2	.0029	1.250	470
5	2.853	6.4666	.7065	.6476	.0589	3.04	76.8	.0085	1.919	700
6	3.300	7.7876	.6856	.6168	.0688	3.78	95.5	.0184	4.093	990
7	3.785	7.2206	.6671	.5793	.0878	3.94	99.5	.0674	17.54	680
8	4.324	8.8345	.6509	.5467	.1042	3.956	100	.0538	61.66	450
9	4.826	8.7656	.6378	.5285	.1093	3.95	99.9	.0589	91.00	360
10	5.359	7.0221	.6229	.5151	.1078			.0574	81.28	220
11	5.758	7.4006	.6095	.4951	.1144			.0640	134.6	(56)

Average = 550

$$w = \frac{[K_{r_1} K_{r_2} + K_{r_2} [H^+] + [H^+]^2] [K_{o_1} K_{o_2} + K_{o_2} [H^+] + [H^+]^2]}{[H^+]^2}$$

$$E'_o = 0.873 + 0.03006 \log \frac{K_{r_1} K_{r_2} + K_{r_2} [H^+] + [H^+]^2}{K_{o_1} K_{o_2} + K_{o_2} [H^+] + [H^+]^2} - 0.0601 \text{ pH}$$

$$E_{h_2} \text{ observed for } [S_o] = 4 \times 10^{-3}; [S_r] = 1.87 \times 10^{-3}$$

$$E'_o - E_{h_2} = 0.03006 \log \frac{[S_r]}{[S_o] - [M]}$$

$$\text{antilog } \frac{E'_o - E_{h_2} - 0.03006 \log \frac{[S_r]}{[S_o]}}{0.03006} = Z = \frac{[S_r] + w K'}{w K'}$$

$$K' = \frac{[S_r]}{w(Z-1)} = 550 \text{ or } \sqrt[3]{K_M} = 1.5 \times 10^3$$

56  
 TABLE 22.—*Wurster's red. Calculations of percentages of maximum merquinone and of merquinone association constant from potential deviations (30°C.)*

$K_{11}=4.8 \times 10^{-4}$ ;  $K_{12}=2.4 \times 10^{-4}$ ;  $K_{01}=4.0 \times 10^{-4}$ ;  $K_{02}=2.0 \times 10^{-4}$ ;  $[S_1]=2.9 \times 10^{-4}$ ;  $[S_0]=4.0 \times 10^{-4}$

Sol. No.	pH	log w	E'	E <sub>h3</sub>	E' - E <sub>h3</sub>	[M] × 10 <sup>6</sup>	%[M]	E' - E <sub>h3</sub> - 0.03006 log $\frac{[S_1]}{[S_0]}$	Z	K' × 10	K <sub>01</sub> × 10 <sup>-47</sup>	$\sqrt{\frac{K_{01}}{K_{02}}} \times 10^{-4}$
2	1.387	3.2530	0.6983	0.6125	0.0858	Neg.	79.1	-0.0001	4.771	3.7	1.21	1.07
2	1.985	3.1286	0.6342	0.5570	0.0768	3.10	91.8	+0.0434	23.47	5.5	1.34	1.10
4	2.436	2.3685	0.6105	0.5124	0.0971	3.53	94.1	+0.0432	91.07	5.3	1.53	1.15
5	2.853	2.7841	0.5909	0.4761	0.1148	3.960	94.8	-0.0349	273.4	5.3	1.53	1.15
6	3.305	2.3053	0.5711	0.4419	0.1292	3.960	94.9	-0.0733	469.4	5.8	1.72	1.06
7	3.907	2.9997	0.5479	0.4177	0.1302	3.991	94.9	-0.0806	839.9	5.6	1.72	1.06
8	4.320	2.7876	0.5214	0.3776	0.1438	3.995	94.9	-0.0870	839.9	5.6	1.72	1.06
9	4.830	2.7304	0.4927	0.3483	0.1444	3.994	94.9	-0.0882	927.6	5.6	1.72	1.06
10	5.365	2.7449	0.4621	0.3170	0.1451	3.996	100.0	-0.0905	1024.0	4.5	2.55	1.37
11	5.770	2.8034	0.4355	0.2931	0.1424	3.996	100.0	-0.0905	1024.0	4.5	2.55	1.37
Averages										5.6 × 10 <sup>-1</sup>	1.38 × 10 <sup>47</sup>	1.10 × 10 <sup>4</sup>

$$w = \frac{[K_{01}K_{12} + K_{02}][H^+] + [H^+]^2}{[H^+]^2} \frac{[K_{01}K_{02} + K_{03}][H^+] + [H^+]^2}{[H^+]^2}$$

$$E' = 0.751 + 0.03006 \log \frac{K_{01}K_{12} + K_{02}}{K_{01}K_{02} + K_{03}} \frac{[H^+] + [H^+]^2}{[H^+] + [H^+]^2} - 0.0001 \text{ pH}$$

$$E_{h3} \text{ observed for } [S_0] = 4 \times 10^{-4}; [S_1] = 2.9 \times 10^{-4}$$

$$E' - E_{h3} = 0.03006 \log \frac{[S_1]}{[S_0]} - [M]$$

$$\text{antilog} \frac{E' - E_{h3} - 0.03006 \log \frac{[S_1]}{[S_0]}}{0.03006} = Z = \frac{[S_1] + wK'}{wK'}$$

$$K' = \frac{[S_1]}{w(Z-1)}$$

$$K_{01} = \frac{1}{(K')^2 K_{01} (K_{02})^2}$$



TABLE 23.—*o*-Tolidine merquinone. Spectrophotometric observations in aqueous solutions at pH 3.8. Read in 10 cm. tube

$\mu$	I. At 3% oxidation				II. At 9% oxidation				III. At 50% oxidation				IV. 100% oxidation: Holoquinone			
	T*	-log T	Calc. to conc. $10^{-4}$	T	-log T	Calc. to conc. $10^{-4}$	T	-log T	T	-log T	Calc. to conc. $10^{-4}$	T	-log T	Calc. to conc. $10^{-4}$	T	-log T
470	84	0.066	0.104	35	0.456	4.65	10	1.000	0	1.155	14.31	0	1.155	14.31	0	1.155
480	84	.104	.460	53	.337	3.44	22	.658	0	1.155	9.42	0	1.155	9.42	0	1.155
490	67	.131	.445	53	.270	2.82	38	.523	7	1.155	7.48	7	1.155	7.48	7	1.155
500	73	.137	.345	58	.277	2.4	38	.430	4	1.155	6.01	4	1.155	6.01	4	1.155
510	68	.195	.425	62	.208	2.1	46	.337	4	1.155	4.82	12	1.155	4.82	12	1.155
520	59	.223	.371	59	.229	2.4	50	.301	19	1.155	4.31	19	1.155	4.31	19	1.155
530	50	.301	.579	58	.237	2.4	52	.284	25	1.155	4.04	25	1.155	4.04	25	1.155
540	45	.347	.575	56	.232	2.6	45	.347	33	1.155	4.97	33	1.155	4.97	33	1.155
550	37	.432	1.040	50	.301	3.1	44	.444	45	1.155	5.11	45	1.155	5.11	45	1.155
560	29	.538	1.36	47	.308	3.4	36	.444	59	1.155	6.35	59	1.155	6.35	59	1.155
570	20	.695	1.76	40	.398	4.1	33	.482	73	1.155	6.90	73	1.155	6.90	73	1.155
580	16	.706	2.01	35	.456	4.7	30	.523	95	1.155	7.48	95	1.155	7.48	95	1.155
590	12	.921	2.32	31	.509	5.2	25	.602	92	1.155	8.61	92	1.155	8.61	92	1.155
600	8	1.067	2.76	29	.538	5.5	23	.638	100	1.155	9.13	100	1.155	9.13	100	1.155
610	6	1.222	3.08	27	.569	5.8	21	.678			9.70			9.70		
620	5	1.301	3.38	26	.585	6.0	18	.745			10.66			10.66		
630	4	1.398	3.52	24	.595	6.32	17	.770			11.02			11.02		
640	4.3	1.367	3.45	26	.585	5.97	20	.699			10.00			10.00		
650	5	1.301	3.28	28	.553	5.6	21	.678			9.70			9.70		
660	7.5	1.125	2.64	31	.509	5.2	27	.569			8.14			8.14		
670	12	.921	2.32	37	.432	4.4	32	.495			7.08			7.08		
680	18	.745	1.88	41	.387	4.0	39	.409			5.85			5.85		
690	25	.602	1.52	49	.310	3.2	44	.351			5.11			5.11		
700	35	.456	1.15	60	.222	2.3	58	.237			3.39			3.39		

\*T = transmission.

TABLE 24.—*p*-Amino dimethyl aniline merquinone and holoquinone. Spectrophotometric observations in aqueous solutions at pH 3.8

$\mu\text{m}$	I. At 25% oxidation				II. At 30% oxidation				III. At 80% oxidation				IV. At 100% oxidation (Holoquinone)	
	T 1 cm.	-log T 1 cm.	-log T 10 cm.	Calc. [M] $10^{-4}$	T 10 cm.	-log T 10 cm.	Calc. [M] $10^{-4}$	T 10 cm.	-log T 10 cm.	Calc. [M] $10^{-4}$	T 10 cm.	-log T 10 cm.	T 10 cm.	-log T
	$[S_1] + [S_2] = 3.12 \times 10^{-4}$ $[S_1] = 7.8 \times 10^{-4}$ $[S_2] = 2.34 \times 10^{-4}$ $[M] \text{ (calc.)} = 7.78 \times 10^{-4}$ $[Hol] \text{ (calc.)} = 2.00 \times 10^{-7}$				$[S_1] + [S_2] = 1.53 \times 10^{-4}$ $[S_1] = 3.8 \times 10^{-4}$ $[S_2] = 7.8 \times 10^{-4}$ $[M] \text{ (calc.)} = 1.00 \times 10^{-4}$ $[Hol] \text{ (calc.)} = 3.4 \times 10^{-7}$				$[S_1] + [S_2] = 1.50 \times 10^{-4}$ $[S_1] = [S_2] = 7.5 \times 10^{-4}$ $[M] \text{ (calc.)} = 6.08 \times 10^{-4}$ $[Hol] \text{ (calc.)} = 1.46 \times 10^{-4}$				$[S_1] + [S_2] = [S_0] = 1.5 \times 10^{-4}$	
470	13	0.886	8.86	1.14	32	0.495	1.15	25	0.002	0.99	25	0.002		
480	12	0.921	9.21	1.18	36	0.444	1.03	26	0.085	0.96	25	0.002		
490	8.5	1.071	10.71	1.38	28	0.553	1.29	19	0.721	1.19	25	0.002		
500	5.0	1.301	13.01	1.67	22	0.658	1.53	15	0.824	1.35	24	0.020		
510	4.75	1.323	13.23	1.70	20	0.721	1.68	13	0.896	1.46	17	0.770		
520	7.5	1.125	11.25	1.45	20	0.699	1.63	11.2	0.951	1.56	18	0.745		
530	7.5	1.125	11.25	1.45	22	0.638	1.53	16	0.796	1.31	19	0.721		
540	6.25	1.204	12.04	1.55	25	0.602	1.40	16.5	0.783	1.29	23	0.638		
550	6.75	1.171	11.71	1.51	20	0.699	1.63	12	0.921	1.51	23	0.648		
560	15	0.824	8.24	1.06	25	0.602	1.25	23	0.796	1.05	22.5	0.638		
570	33	0.482	4.82	0.62	39	0.409	0.95	36	0.638	0.73	33	0.482		
580	50	0.301	3.01	0.39	45	0.347	0.81	51	0.444	0.48	45	0.347		
590	67	0.174	1.74	0.22	52	0.284	0.66	59	0.229	0.38	60	0.282		
600	88	0.066	0.66	0.07				60	0.222	0.37		0.222		

[S] =  $1.04 \times 10^{-4}$

TABLE 25.—(Curve C, Fig. 7)—Wurster's red. Calculation of percentage maximum merquinone at various pH values when  $[S_2] = 4.04 \times 10^{-4}$  and  $[S_0] = 1 \times 10^{-3}$ 

pH	$[H^+]^p$	$K_a[H^+]^p$	z	$K_{ad}[H^+]^p$	y	log w	$K'_w$	$K'_w + [S_2] + [S_0]$	$(A)^2$	$\sqrt{(A)^2 - 4[S_2][S_0]}$	$[M] \times 10^4$	Per cent of max. [M]
1.0	$1.0 \times 10^{-4}$	$2.4 \times 10^{-4}$	$1.0240001 \times 10^{-3}$	$2.0 \times 10^{-4}$	$1.002 \times 10^{-4}$	$2.0111677$	$5.74557 \times 10^{-3}$	$6.15987 \times 10^{-3}$	$3.79440 \times 10^{-3}$	$6.15855 \times 10^{-3}$	0.66	6.6
1.2	$3.982 \times 10^{-5}$	$1.5144 \times 10^{-4}$	$4.133441 \times 10^{-3}$	$1.262 \times 10^{-4}$	$3.99462 \times 10^{-5}$	$3.6176858$	$2.32108 \times 10^{-3}$	$2.73506 \times 10^{-3}$	$7.48055 \times 10^{-3}$	$2.73210 \times 10^{-3}$	1.48	14.8
1.4	$1.585 \times 10^{-5}$	$9.5544 \times 10^{-5}$	$1.9805452 \times 10^{-3}$	$7.962 \times 10^{-5}$	$1.592962 \times 10^{-5}$	$3.2276357$	$9.45853 \times 10^{-4}$	$1.598533 \times 10^{-3}$	$1.84920 \times 10^{-3}$	$1.35390 \times 10^{-3}$	2.98	29.8
1.6	$6.310 \times 10^{-6}$	$6.0288 \times 10^{-5}$	$6.9128920 \times 10^{-4}$	$5.024 \times 10^{-5}$	$6.36024 \times 10^{-6}$	$4.8431039$	$3.90203 \times 10^{-4}$	$8.04204 \times 10^{-4}$	$6.46744 \times 10^{-4}$	$7.94093 \times 10^{-4}$	5.06	50.6
1.8	$2.512 \times 10^{-6}$	$3.8040 \times 10^{-5}$	$2.8924115 \times 10^{-4}$	$3.170 \times 10^{-5}$	$2.5437 \times 10^{-6}$	$4.4657065$	$1.64019 \times 10^{-4}$	$5.78019 \times 10^{-4}$	$3.34108 \times 10^{-4}$	$5.63867 \times 10^{-4}$	7.08	70.8
2.0	$1.0 \times 10^{-6}$	$2.4 \times 10^{-6}$	$1.2400115 \times 10^{-4}$	$2.0 \times 10^{-6}$	$1.02 \times 10^{-6}$	$4.1020258$	$7.06294 \times 10^{-5}$	$4.84829 \times 10^{-5}$	$2.3506 \times 10^{-5}$	$4.67868 \times 10^{-5}$	8.48	84.8
2.2	$3.9816 \times 10^{-7}$	$1.5144 \times 10^{-6}$	$5.49612 \times 10^{-5}$	$1.262 \times 10^{-6}$	$4.1078 \times 10^{-7}$	$5.7539079$	$3.17538 \times 10^{-5}$	$4.45754 \times 10^{-5}$	$1.9570 \times 10^{-5}$	$4.27247 \times 10^{-5}$	9.26	92.7
3.0	$1.0 \times 10^{-7}$	$2.4 \times 10^{-7}$	$3.40115 \times 10^{-6}$	$2.0 \times 10^{-7}$	$1.2 \times 10^{-7}$	$6.6108670$	$2.28557 \times 10^{-6}$	$4.16296 \times 10^{-6}$	$1.73294 \times 10^{-6}$	$3.96401 \times 10^{-6}$	9.95	99.6
5.0	$1.0 \times 10^{-10}$	$2.4 \times 10^{-10}$	$2.5232 \times 10^{-10}$	$2.0 \times 10^{-10}$	$2.108 \times 10^{-10}$	$7.7261664$	$2.98065 \times 10^{-7}$	$4.14298 \times 10^{-7}$	$1.71643 \times 10^{-7}$	$3.94313 \times 10^{-7}$	9.993	100.0

$$K_a = 4.8 \times 10^{-4}$$

$$K_{ad} = 2.4 \times 10^{-4}$$

$$K_{ad} = 4. \times 10^{-4}$$

$$K_{ad} = 2. \times 10^{-4}$$

$$z = K_a K_a + K_a [H^+] + [H^+]^2$$

$$y = K_a K_a + K_a [H^+] + [H^+]^2$$

$$w = \log [H^+]^p$$

$$K'_w = 5. \times 10^{-4}$$

$$2[M] = [S_2] + [S_0] + K'_w - \sqrt{([S_2] + [S_0] + K'_w)^2 - 4[S_2][S_0]}$$

## VIII. References

Previous papers in the series: Studies on Oxidation-Reduction:

- I. Introduction. W. Mansfield Clark. Public Health Reports, 1923, **38**, 443. (Reprint No. 823.)
  - II. An analysis of the theoretical relations between reduction potentials and pH. W. Mansfield Clark and Barnett Cohen. Public Health Reports, 1923, **38**, 666. (Reprint No. 826.)
  - III. Electrode potentials of mixtures of 1-naphthol-2-sulphonic acid indophenol and the reduction product. W. Mansfield Clark and Barnett Cohen. Public Health Reports, 1923, **38**, 933. (Reprint No. 834.)
  - IV. Electrode potentials of indigo sulphonates, each in equilibrium with its reduction product. M. X. Sullivan, Barnett Cohen, and W. Mansfield Clark. Public Health Reports, 1923, **38**, 1669. (Reprint No. 848.)
  - V. Electrode potentials of simple indophenols, each in equilibrium with its reduction product. Barnett Cohen, H. D. Gibbs, and W. Mansfield Clark. Public Health Reports, 1924, **39**, 381. (Reprint No. 904.)
  - VI. A preliminary study of indophenols: (A) Dibromo substitution products of phenol indophenol; (B) Substituted indophenols of the ortho type; (C) Miscellaneous. Barnett Cohen, H. D. Gibbs, and W. Mansfield Clark. Public Health Reports, 1924, **39**, 804. (Reprint No. 915.)
  - VII. A study of dichloro substitution products of phenol indophenols. H. D. Gibbs, Barnett Cohen, and R. K. Cannan. Public Health Reports, 1925, **40**, 649. (Reprint No. 1001.)
  - VIII. Methylene blue. W. Mansfield Clark, Barnett Cohen, and H. D. Gibbs. Public Health Reports, 1925, **40**, 1131. (Reprint No. 1017.)
- Bach, A. (1915): Kommt Peroxydase in Hefen vor? *Fermentforschung*, **1**, 197.
- Battelli, F., and Stern, L. (1912): Einfluss verschiedener Faktoren auf die Oxydation des p-Phenylendiamins durch die Tiergewebe. *Biochem. Z.*, **46**, 343.
- Bay, E. C. C., and Stewart, A. W. (1906): The relation between absorption spectra and chemical constitution. Part II. The  $\alpha$ -diketones and quinones. *J. Chem. Soc.*, **89**, 507.
- Biilmann, E. (1920): Sur l'hydrogenation des quinhydrones. *Ann. Chim.*, **15**, 109.
- Clark, M. (1925): Recent studies on reversible oxidation-reduction in organic systems. *Chem. Rev.*, **2**, 127.
- Conant, J. B., and Fieser, L. F. (1922): Free and total energy changes in the reduction of quinones. *J. Am. Chem. Soc.*, **44**, 2480.
- Ellms, J. W., and Hauser, S. J. (1913): Ortho-tolidine as a reagent for the colorimetric estimation of small quantities of free chlorine. *J. Ind. Eng. Chem.*, **5**, 915, 1030.
- Granger, F. S., and Nelson, J. M. (1921): Oxidation and reduction of hydroquinone and quinone from the standpoint of electromotive-force measurements. *J. Am. Chem. Soc.* **43**, 1401.
- Griess, P., and Duisberg, C. (1889): Ueber Benzidin- und Benzidinsulfon-sulfosäuren. *Ber.*, **22**, 2459.
- Hantzsch, A. (1916): Über meri-chinoide Salze. *Ber.*, **49**, 511.
- Hantzsch, A. (1917): Über den Einfluss von Lösungsmitteln auf die Lichtabsorptions gelöster Stoffe. *Ber.*, **50**, 1413.

- Hartley, W. L. *et al* (1902): Absorption spectra and chemical constitution of organic substances. Report British Assoc. Adv. Sci. pp. 99-119.
- Hastings, A. B., and Van Slyke, D. D. (1922): The determination of the three dissociation constants of citric acid. *J. Biol. Chem.*, **53**, 269.
- Klingstedt, F. W. (1923): Spectre d'absorption ultraviolet de la paraquinone. *Compt. rend.*, **176**, 1550.
- Kolthoff, I. M. (1924): Over het gebruik van benzidine als reagens en tevens als indicator voor een bepaalde oxydatie-potentiaal. *Chem. Weekblad*, **21**, 2.
- LaMer, V. K., and Baker, L. E. (1922): The effect of substitution on the free energy of oxidation-reduction reactions. I. Benzoquinone derivatives. *J. Am. Chem. Soc.*, **44**, 1954.
- Lane-Clayton, J. E. (1916): *Milk and its hygienic relations*. London.
- Lewis, G. N., and Randall, M. (1923): *Thermodynamics and the free energy of chemical substances*. New York.
- Lifschitz, J. (1916): Zur Kenntnis der Chinhydrone. *Ber.*, **49**, 2050.
- Lifschitz, J. (1916): Studien über Chromophorfunktion. *Z. wiss. Photo.*, **16**, 101, 140, 149.
- Lifschitz, J. (1917): Über den Sättigungszustand von Chromophoren. *Ber.*, **50**, 906.
- Lifschitz, J., and Jenner, F. W. (1915): Chromoisomere Salze und Chromoester aus p-Nitro-benzyleyanid. *Ber.*, **48**, 1730.
- Orla Jensen (1906): De l'origine des oxydases et réductases du lait de vache. *Rev. gen. Lait*, **6**, 34, 56, 85.
- Partington, J. R. (1925): Book review. *J. phys. chem.*, **29**, 494.
- Pfeiffer, P. (1914): Zur Konstitution der Chinhydrone. *Ann.*, **404**, 1.
- Pfeiffer, P. (1917): Färbige organische Molekülverbindungen. *Ann.*, **412**, 253
- Pratt, D. S., and Gibbs, H. D. (1913): The absorption spectra of phenoquinone, 2, 5-dianilinoquinone, 2, 5-dianilinoquinone anil, and 2, 5-dianilinoquinone-dianil (azophenine). *Philippine J. Sci.*, **8**, 51.
- Schlenk, W. (1909): Ueber die Natur der Chinhydrone und der Triphenylmethanfarbstoffe. *Ann.*, **368**, 277.
- Schlenk, W., and Knorr, A. (1908): Ueber chinoide Biphenyl-derivate. *Ann.*, **363**, 313.
- Sørensen, S. P. L., Sørensen, M., and Linderstrøm-Lang, K. (1921): Sur l' "erreur de sel" inhérente à l'électrode de quinhydrone. *Compt. rend. Lab. Carlsberg*, **14**, 1.
- Stieglitz, J. (1924): A theory of color production. Address, The Franklin Institute, Philadelphia.
- Sudborough, J. J. (1916): Additive compounds of trinitrobenzene. *J. Chem. Soc.*, **109**, 1339.
- VanSlyke, D. D. (1922): On the measurement of buffer values and on the relationship of buffer value to the dissociation constant of the buffer and the reaction of the buffer solution. *J. Biol. Chem.* **52**, 525.
- Willstätter, R., and Mayer, E. (1904): Ueber Chinondiimid. *Ber.*, **37**, 1494.
- Willstätter, R., and Pfannenstiel, A. (1905): Ueber die Imine des Chinons III. *Ber.*, **37**, 4605.
- Willstätter, R., and Piccard, J. (1908): Über die Farbsalze von Wurster. *Ber.*, **41**, 1458.
- Wurster, C., and Sendtner, R. (1879): Zur Kenntniss des Dimethylparaphenylendiamins. *Ber.*, **12**, 1803.





